HYPERBRANCHED CONJUGATED POLYMERS: AN INVESTIGATION INTO THE SYNTHESIS, PROPERTIES AND POSTFUNCTIONALIZATION OF HYPERBRANCHED POLY(PHENYLENE VINYLENE-PHENYLENE ETHYNYLENE)S

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Christopher Kub

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Approved by:

Dr. Uwe Bunz, Advisor
School of Chemistry and Biochemistry
Georgia Institute of Technology

Dr. Laren Tolbert
School of Chemistry and Biochemistry
Georgia Institute of Technology

Dr. David Collard
School of Chemistry and Biochemistry
Georgia Institute of Technology

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LIST OF SYMBOLS AND ABBREVIATIONS

abs	absorbance
AFP	amplifying fluorescent polymer
a.u.	arbitrary units
cm	centimeter
DB	degree of branching
DCM	dichloromethane
dL	decaliter
DI	distilled
DNA	deoxyribonucleic acid
em	emission
H^1	proton
HCPs	hyperbranched conjugated polymers
HBP	hyperbranched polymer
Hz	hertz
FHCP	fluorescent conjugated hyperbranched polymer
Fl.	fluorescense
F_0	fluorescence intensity without added quencher
$F_{[Q]}$	fluorescence intensity in the presence of quencher
FTIR	fourier transform infrared
GPC	gel permeation chromatography
IR	infrared
K	kelvin

K_{sv}	stern-volmer constant
L	liter
MHz	megahertz
MeOH	methanol
M_n	number-average molecular weight
mol	mole
M_w	weight-average molecular weight
M_z	z-average molecular weight
NBS	n-bromosuccinimide
nm	nanometer
NMR	nuclear magnetic resonance
PAE	poly(arylene ethynylene)
PMT	photomultiplier tube
P_n	degree of polymerization
PPE	poly(phenyleneethynelene)
Q	quencher
ROMP	ring-opening metathesis polymerization
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TMS	trimethylsilyl
UV	ultraviolet
UV-vis	ultraviolet-visible
wt	weight
ε	molar absorptivity

η_{sp}	specific viscosity
Φ	quantum yield

SUMMARY

There are two general ways to introduce functionalities into a polymeric structure: functionalization of the monomeric units before polymerization and postfunctionalization of the preformed polymer. Building libraries of polymers with different functionalities can be completed with significantly less effort by the second method, as each postfunctionalization of a single batch of polymeric backbone can involve as little as one synthetic step.

One method of building a polymeric backbone for postfunctionalization involves the synthesis of hyperbranched conjugated polymers (HCPs) from AB_2 monomeric units. A polymer formed from *n* AB_2 monomeric units should contain *n* reactive B groups, which act as sites of functionalization. Utilizing this principle, two different hyperbranched poly(phenylene vinylene-phenylene ethynylene) scaffolds were synthesized and studied in both their inherent properties and functionalization.

The first HCP synthesized was compared against a monomeric cruciform model and a linear polymer with a similar structure. The hyperbranched polymer has red-shifted absorption and emission in comparison to the cruciform model and linear polymer. The HCP quenches paraquat more efficiently than the linear polymer by a factor of about two, suggesting a greater rate of energy transfer.

The functionalization of HCPs was studied; iodine groups decorating the HCPs were replaced with terminal alkynes by Pd-catalyzed coupling, providing a library of 24 differently functionalized HCPs. Elemental analyses of the postfunctionalized polymers show nearly complete substitution of the iodine groups. The postfunctionalized polymers

show increased fluorescence compared to the original iodine decorated polymers, due to the loss of the heavy atom effect inducing iodine groups. The emissions of the postfunctionalized polymers in solution show a strong dependence on the groups attached to the conjugated structures, with emission maxima ranging from 505 nm to 602 nm; quantum yields range from 0.7% to 25%. Solid-state emission studies show stronger and more red-shifted spectra compared to emissions observed in solution.

CHAPTER 1

INTRODUCTION

From a general perspective of polymer chemistry there are two ways to introduce functionalities into a polymeric structure: functionalization of the monomeric units, or postfunctionalization of a preformed polymer. The first method requires significantly more synthetic effort if libraries of polymers are desired, because each polymer starts from its own monomer. Therefore, efficient postfunctionalization pathways are of great interest in terms of economy and versatility. Weck and coworkers[1] have used ring-opening metathesis polymerization (ROMP) of functionalized norborenes and cyclooctenes to create universal polymeric backbones containing supramolecular connectors. The postfunctionalization of these universal polymeric backbones by addition of molecules with complementary functionality to the supramolecular connectors enables the preparation of a host of new polymers.

In conjugated polymers, such as poly(*para*-phenylene ethynylene)s (PPEs),[2] an efficient postfunctionalization should allow for manipulation of the electronic structure of the backbone. However, in most cases, postfunctionalizations do not directly affect the electronic structures of polymer backbones because the reactions occur on nonconjugated side chains. This is the case with Weck's universal polymer backbone, LeClerc's[3] postfunctionalized polythiophenes and PPEs postfunctionalized through 1,3-dipolar cycloaddition of azides to alkynes.[4]

Inherently, hyperbranched polymers[5] (HBPs) offer a posibility for

postfunctionalization, as a polymer formed from *n* AB_2 units will provide a remaining number of *n* reactive B groups. Described from a theoretical point of view as an intermolecular condensation of AB_x monomers by Flory in 1952,[6] HBPs have been exploited over the last several years in live-cell imaging,[7] solar cells,[8] drug delivery systems,[9] and surface chemistry.[10] Postfunctionalization of fluorescent HBPs presents an opportunity to affect the electronic structure of their conjugated backbones, providing great possibilty for their use in sensing.

Fluorescent hyperbranched conjugated polymers (FHCPs) can be used in sensing applications, as their fluorescense and conjugated character allow for high sensitivity toward analytes. Fluorescent polymers can be useful in sensing because they may change their signal when in contact with analytes. Conjugation allows for amplification of signal because conjugation of a polymer backbone extends the area that a single quencher can act in changing a signal.[11]

Linear fluorescent conjugated polymers have been studied extensively and used for a variety of sensory purposes, including the detection of explosives, metal cations, proteins, and DNA.[12-15] They are, however, limited by their two-dimensional character. HCPs and other three-dimensional conjugated polymeric systems allow for increased surface contact with target analytes and their branched character allows for multiple diffusion pathways for exciton transport. Whereas on a linear conjugated polymer an exciton travels in a one-dimensional random walk and will visit a particular receptor many times, in a branched structure an exciton has more possible pathways for vectorial transport of an exciton toward a receptor in contact with an analyte, allowing an exciton to be effected by more receptors, increasing

amplification.[11] Swager and coworkers have demonstrated that aggregates and thin films have increased sensitivity towards analytes compared to linear polymers, due to this effect.[16]

Dendrimers and HCPs are three-dimensional structures and may be preferable to aggregates and thin-films for sensing, as aggregates and thin films are insoluble and lack well-defined character. Moore and coworkers[17] have developed symmetrical *meta*-substituted dendritic PPEs that efficiently collect and transport energy. They showed that their *meta*-PPE dendrimers have an increasing ability to act as light harvesters with increasing generation number, and that these light harvesters efficiently transfer energy to a core with or without perylene, due in part to the energy gradient that results from increasing conjugation lengths closer to the core. Peng and coworkers[18] have built unsymmetrical branching PPE dendrimers that have substantially different photophysical properties than Moore's symmetrical PPE dendrimers. The unsymmetrical *ortho/para* branching gives larger and more diverse conjugation lengths due to the reduction of π-conjugation-breaking *meta*-linkages, resulting in broader absorption spectra for higher generation unsymmetrical PPE dendrimers, increased light absorption, increased energy gradients towards the core, and an overall red-shifting of emission.

Dendrimers are better defined than HCPs and may have improved solublity; however, they require costly multi-step syntheses. HCPs have many of the advantages of dendrimers while requiring much shorter and simpler syntheses. Moore and coworkers[19] have developed *meta*-substituted hyperbranched PPEs and studied their physical properties; including self-limited growth and crosslinking. Using higher

ratios of core molecule to monomer allowed for an increase in the degree of polymerization and reduction in polydispersity. Weder and coworkers[21] recently synthesized hyperbranched PPEs without the communication problems inherent in *meta*-substituted PPEs. The highly soluble *ortho/para* substituted hyperbranched PPEs show typical optical properties for highly-conjugated linear PPEs. They designed solutions to the overly rapid polymerization of their HCPs by using less reactive tribromobenzene, instead of triiodobenzene. After polymerization, unreacted ethynyl groups presented some problem, due to problems with cyclotri- and [4+2] cylcodimerization crosslinking, resulting in insoluble materials. Unreacted ethynyl groups were postfunctionalized by Sonogashira coupling with end-capper 4-iodotoluene.

This thesis expands upon work on the postfunctionalization of polymers and the development of linear PPEs, dendritic PPEs and hyperbranched PPEs. It develops low polydispersity, high degree of polymerization, soluble and processible three-dimensional fluorescent hyperbranched *ortho/para* substituted conjugated polymers of high sensitivity which retain decorating iodine groups, allowing for postfunctionalization able to affect the electronic structure of the conjugated backbones.

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CHAPTER 2

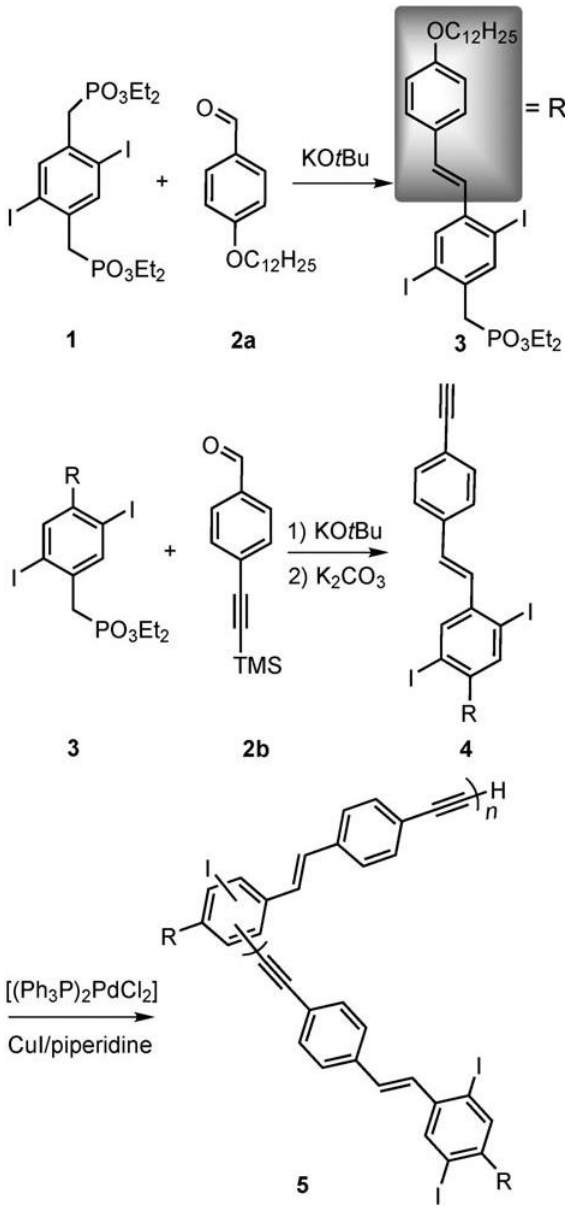
SYNTHESIS AND PROPERTIES OF HYPERBRANCHED CONJUGATED POLYMERS

2.1 Abstract

This chapter describes the synthesis of a hyperbranched poly(phenylene vinylene-phenylene ethynylene) scaffold, along with monomeric and linear polymer models. It compares the three forms in absorbance, emission and quantum yield; as well, it compares the linear and hyperbranched polymers in rate of energy transfer. This chapter further describes some initial postfunctionalizations of the hyperbranched polymer, introducing an area of research described thoroughly in Chapter 3.

2.2 Results and Discussion

A Horner reaction of **1** with **2a** furnishes **3**, which, after a second Horner reaction with **2b** and subsequent deprotection gives the monomer **4**. Classic Sonogashira polymerization of **4** in a mixture of THF and piperidine with CuI as co-catalyst furnishes the hyperbranched polymer **5** in 87% yield, with a molecular weight of 2.4×10^4 and a polydispersity index M_w/M_n of 2.0(Shown in Figure 2.1). In a similar fashion, the model compound **7** and the linear conjugated polymer **6** (M_n=2.5×10^4, M_w/M_n=2.5, Figure 2.2) were prepared (see 2.3.2 Synthesis). By coincidence, both polymers had similar molecular weights, which allowed a comparison of their intrinsic viscosity in chloroform, namely $[\eta] = 0.19$ dLg^{-1} for **5** and $[\eta] = 0.32$ dLg^{-1} for **6**.



Scheme 2.1. Synthesis of the hyperbranched polymer **5**.

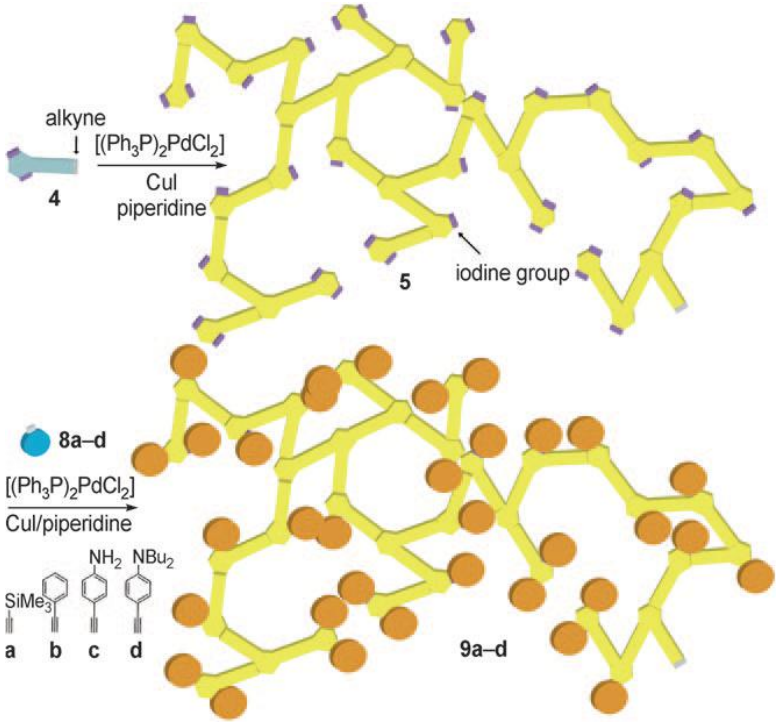
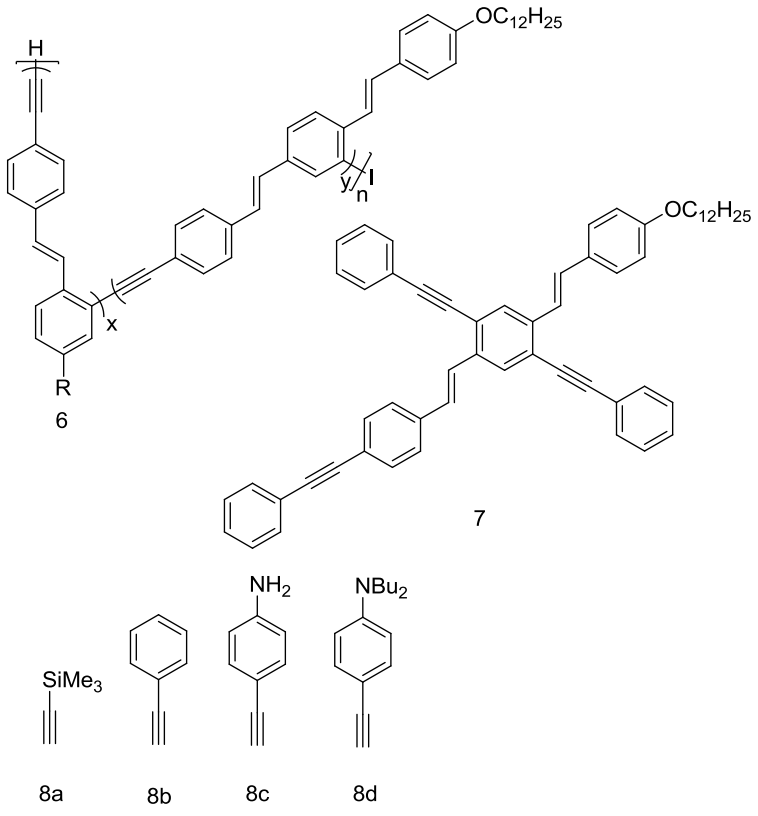


Figure 2.1. Synthesis and palladium-catalyzed postfunctionalization of **5**.



Scheme 2.2. Linear polymer **6** and model compound **7** along with alkynes **8a-8d** used for postfunctionalization.

As expected, solutions of the hyperbranched polymer **5** are less viscous than those of a linear polymer with the same molecular weight. As **5** contains one iodine atom per repeat unit (17.5% iodine by combustion analysis) its fluorescence is quenched by the heavy atom effect (Figure 2.2), but **5** is freely soluble in dichloromethane and chloroform. A Sonogashira coupling of **5** with **8a-8d** was performed (Figure 2.1) to obtain **9a-9d** as yellow or orange powders after standard workup, in yields that ranged from 84%-97% (Table 2.1). From combustion analysis, the polymers that formed had iodine content between 0.2 and 0.5 wt%, indicating efficient substitution. For **9a-9db**, the quantum yields of emission were increased by a factor of 3-10 (Table 2.1) as a consequence of the removal of the iodine groups. The emission wavelength changed from 510 nm in **5** to 553 nm in **9d**, documenting a significant red shift of emission upon functionalization. The addition of a donor group, as represented by the dibutylaniline unit in **9d**, has the strongest bathochromic effect upon emission. The position of the absorption maxima of **5** and **9a-9d** are almost unaffected and vary from 386 to 397 nm. Figure 2.2 shows representative solutions of the model compound **7**, the linear polymer **6**, **5**, and **9a-9d** (corresponding spectra are given in 2.3.3 Supplemental Data). It is important to note that all the hyperbranched polymers show a red-shifted absorption and emission relative to **6** and to the model **7**.

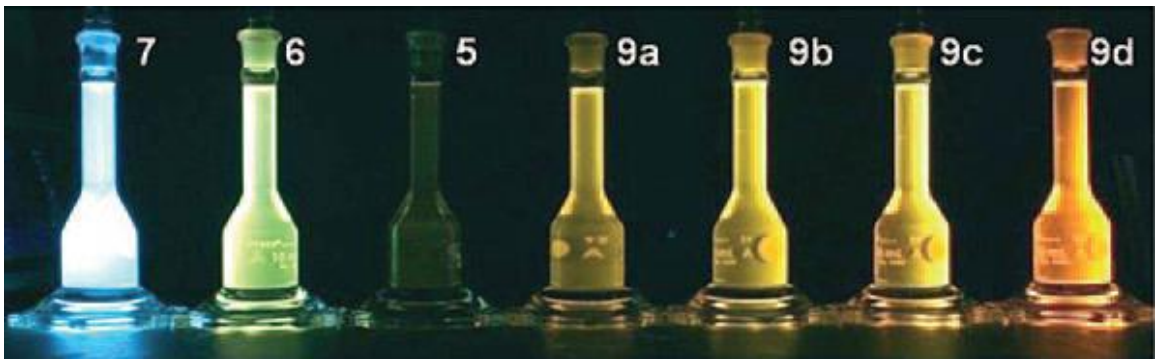


Figure 2.2. Solutions of **5-7** and **9a-9d** in dichloromethane under a black light (λ_{max} = 365 nm) at a concentration of 10^{-5} mol L^{-1}.

Table 2.1. Optical properties of **5-7** and **9a-9d**

	λ_{max} abs[a]	λ_{max} em[a]	*Φ[%]*	ε[b]	Yield [%]
7	337, 389	472	87	39800	na
6	380	500	30	66450	na
5	392	510	3	84000	na
9a	397	513	25	43600	97
9b	397	519	19	32600	84
9c	386	528	13	60700	89
9d	382	553	16	65600	85

[a] Maximum wavelength for absorption and emission in nm; all measurements carried out in dichloromethane. [b] ε in $Lmol^{-1}cm^{-1}$ per repeat unit for the polymers.

It was of interest to establish whether **9** could also give rise to blue-shifted emission. Upon protonation of **9d**, the solution gives green emission (λ_{max} (em) = 487 nm) and an absorption maximum of λ_{max} (abs) = 346 nm, suggesting that the optical properties of hyperbranched PAEs **9** can be engineered not only to be more red-emissive, but also into blue- or green-emissive materials. Protonation is not only an excellent way to shift the electronic properties of the prepared hyperbranched polymers, but it also indicates that the introduction of electronegative residues into the hyperbranched polymers should lead to hypsochromically shifted derivatives of **9**.

An attractive aspect of the hyperbranched conjugated polymers is their branched character, which should increase the rate of energy transfer, as a general matter of structural principle.[1] A useful tool to test these polymers for increased energy transfer through branching is the quenching of their fluorescence by paraquat. Swager et al.[2] demonstrated that quenching of conjugated polymers of the PPE type by paraquat displays an approximately 80-fold increased efficiency in comparison to that of small molecules, which is a result of the molecular-wire

effect. The factor of 80 is the maximum number of monomer units that is sampled by a single exciton in a linear chain. Branching should increase the efficiency of an exciton to sample polymer chains. Figure 2.3 shows the quenching of **9b** and linear polymer **6** by paraquat. The Stern-Volmer equation is used, with $F_0/F_{[Q]} = K_{sv}[Q] + 1$, where F_0 denotes the fluorescence intensity without added quencher Q, $F_{[Q]}$ is the fluorescence intensity of the solution in the presence of the concentration [Q] of the quencher Q, and K_{sv} is the Stern-Volmer constant.[3] In this equation, the easily measured total concentration of quencher [Q] is used as an approximation for its free concentration; for the condition [fluorophore][K_{sv}] < 1, this approximation holds well, and K_{sv} values of 2.0×10^2 and 4.1×10^2 result. These K_{sv} values are low, as there is not binding element engineered into either **9b** or **6**. However, the hyperbranched polymer **9b** is more efficiently quenched by paraquat than **6** by a factor of about two. The two values are able to be compared, as the molecular weights of the two polymers are approximately equal and their degree of polymerization is considerably below $P_n < 80$. In hyperbranched polymers of higher molecular weight, this effect should be even more distinctive.

2.3 Experimental Section

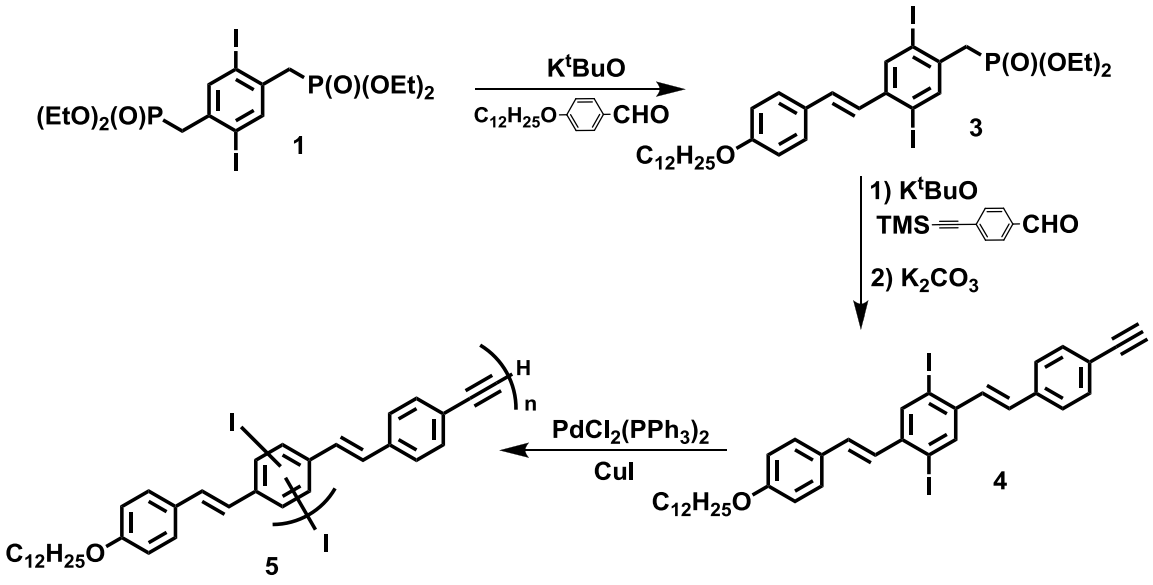
2.3.1 Materials and Methods

All chemicals were purchased from Aldrich Chemical, Acros, TCI America, or Fischer Scientific and used without purification unless otherwise specified. Column chromatography was performed using Standard Grade silica gel 60 Å, 32-63 μm (230 x 450 mesh) from Sorbent Technologies and the indicated eluent. Elution of conjugated compounds was readily monitored using a handheld UV lamp (365 nm). Melting points were obtained using a Mel-Temp apparatus fitted with a Fluke 51K/J digital thermometer. All IR spectra were obtained using a Shimadzu FTIR-8400s spectrometer. Unless otherwise specified, NMR spectra were recorded at 298 K on a

Varian Mercury spectrometer (300 MHz). Chemical shifts are reported in parts per million (ppm), using residual solvent (chloroform-*d*) as an internal standard (δ = 7.26 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, and integration. Mass spectral analyses were provided by the Georgia Institute of Technology Mass Spectrometry Facility. GPC experiments were performed using a Shimadzu LC-10AT chromatographer with polystyrene standards for the molecular weights. Elemental analysis of the compounds was provided by Columbia Analytical Services.

All absorption spectra were collected using a Shimadzu UV-2401PC spectrophotometer. All emission spectra were acquired using a PTI LPS-220B spectrofluorophotometer. Quantum yields for the models and polymers were measured using standard procedures. In all cases, quinine sulfate was used as a standard and all solutions were purged with nitrogen prior to measurement. Pictures of luminescent solutions were taken with a Canon EOS 30D.

2.3.2 Synthesis



Scheme 2.3. Synthesis of the hyperbranched polymer.

Monophosphonate 3 (General Procedure for Horner Monoalkenylation A): A solution of diphosphonate **1**[5] (6.67 g, 10.7 mmol) in dry THF (100 mL) was stirred at 0ºC under N_2 and ^{t}BuOK (1.08 g, 9.67 mmol) was added carefully. After addition, the reaction mixture was stirred for 3 min. Then, 4-dodecyloxybenzaldehyde **2a** (2.50 g, 8.59 mmol) in dry THF (15 mL) was added as quickly as possible. After 30-40 min, 100 mL of water, followed by 5 mL of a saturated solution of NH_4Cl, were added to quench the reaction. The mixture was extracted with DCM (3 x 100 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the crude mixture was purified by column chromatography (ethyl acetate / hexane 1:2) to give a yellow solid. (2.75 g, 42%)

Mp: 56.5-58.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.88 (t, 3H, J = 6 Hz); 1.24-1.40 (m, 22H); 1.40-1.52 (m, 2H); 1.74-1.86 (m, 2H); 3.32 (d, 2H, *J* = 22 Hz); 3.97 (t, 2H, *J* = 12 Hz); 4.04-4.14 (m, 4H); 6.84-7.02 (m, 4H); 6.85-7.02 (m, 4H); 7.45 (d, 2H, *J* = 9 Hz); 7.86 (d, 1H, *J* = 3 Hz); 8.00 (d, 1H, *J* = 1 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.7; 141.3 (d, *J* = 4Hz); 140.9 (d, *J* = 5 Hz); 136.4 (d, *J* = 3 Hz); 136.0 (d, *J* = 9 Hz); 132.4; 129.3; 128.5; 128.2; 115.0; 101.4 (d, *J* = 9 Hz); 99.8 (d, *J* = 5 Hz); 68.3; 62.7 (d, *J* = 7 Hz); 37.7 (d, *J* = 137 Hz); 36.8; 32.2; 29.9; 29.9; 29.8; 29.8; 29.6; 29.6; 29.5; 26.3; 22.9; 16.7; 16.6; 14.4.

IR (cm^{-1}): 3475, 3031, 2916, 2850, 1747, 1604, 1577, 1512, 1465, 1245, 1026, 960, 794.

Asymmetric monomer 4 (General Procedure B): A solution of **3** (6.25 g, 8.15 mmol) and 4-((trimethylsilyl)ethynyl)benzaldehyde **2b** (1.65 g, 8.15 mmol) in dry THF (85 mL) was stirred at

0ºC under N_2 while ^{t}BuOK (1.05 g, 9.38 mmol) was added carefully. After addition, the reaction mixture was stirred for 30 min. Then, 30 mL of methanol followed by 1.50 g (10.8 mmol) of K_2CO_3 were added. The mixture was stirred at room temperature for 3 h. The reaction mixture was then poured into water and extracted with DCM (3 x 80 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the crude mixture was purified by column chromatography (hexanes / dichloromethane 9:1) to give a yellow solid. (3.36 g, 56%)

Mp: 148.0-150.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.88 (t, 3H, *J* = 6 Hz); 1.24-1.40 (m, 16H); 1.40-1.52 (m, 2H); 1.74-1.86 (m, 2H); 3.16 (s, 1H); 3.98 (t, 2H, *J* = 7 Hz); 6.89-7.02 (m, 5H); 7.20 (d, 1H, *J* = 16 Hz); 7.47 (d, 2H, *J* = 9 Hz); 7.49 (broad s, 4H); 8.05 (s, 2H)

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.8; 141.6; 140.1; 137.3; 136.6; 136.2; 132.8; 132.4; 131.8; 131.3; 129.3; 128.5; 128.2; 127.0; 122.0; 115.0; 100.7; 100.4; 83.8; 78.6; 68.4; 32.2; 29.9; 29.8; 29.6; 29.6; 29.5; 26.3; 22.9; 14.4.

IR (cm^{-1}): 3267, 3031, 2920, 2846, 2098, 1797, 1604, 1512, 1469, 1450, 1284, 1245, 1176, 1029, 956, 621.

MS (EI): (M^+) 742.2

Polymer 5 (General Procedure for Polymerization C): A solution of **3** (2.14 g, 2.88 mmol) in 18 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk flask, degassed and stirred under N_2 for 5 min at room temperature. The catalyst mixture, $PdCl_2(PPh_3)_2$ (9.9 mg, 14 μmol) and CuI (3.0 mg, 14 μmol), was added; the reaction was sealed, warmed to 40 ºC and

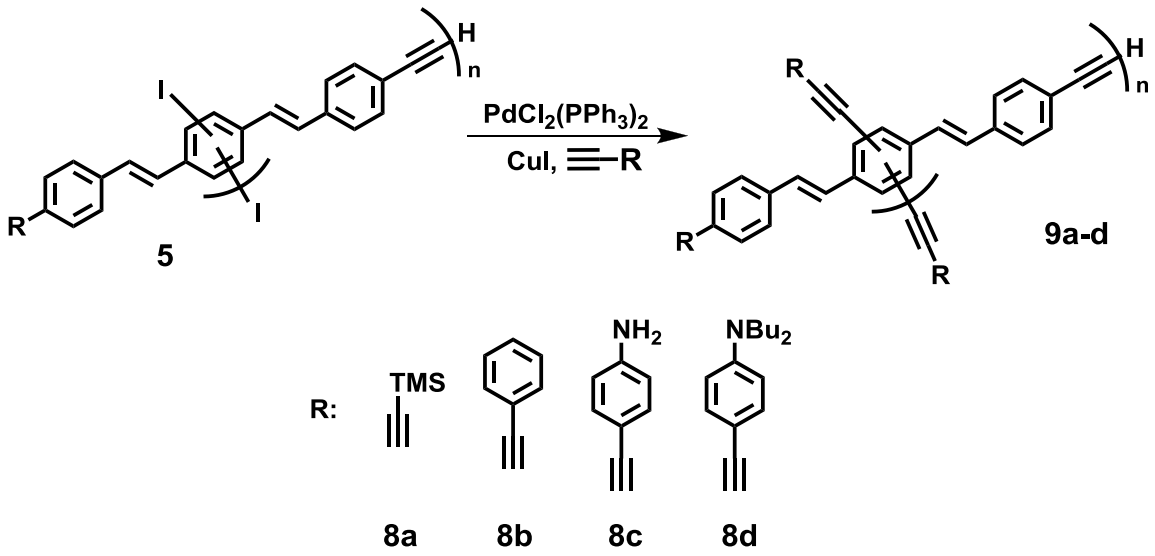
stirred at that temperature for 5 days. Methanol was added to precipitate the polymer, which was filtered off and washed several times with methanol to give a yellow solid. (1.53 g, 87%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-1 (br m, 3nH); 1-1.6 (br m, 18nH); 1.6-2 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.4-7.7 (m, 14nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.2; 139.7; 136.5; 132.4; 132.3; 129.2; 128.8; 128.5; 127.1; 122.4; 115.0; 100.8; 95.9; 89.6; 68.3; 32.2; 29.9; 29.7; 26.3; 22.9; 14.4.

IR (cm^{-1}): 3031, 2920, 2850, 2202, 1604, 1512, 1249, 1172, 956, 852; 813, 528.

Elem. Anal. C, 70.05%; H, 5.48%; I, 17.5% (calc. C, 70.12%; H, 6.44%; I, 20.58%)



Scheme 2.4. Postfunctionalization of the polymer.

Polymer 9c (General Procedure D): A solution of polymer **5** (92 mg, 0.15 mmol), $PdCl_2(PPh_3)_2$ (2.1 mg, 3 μmol) and CuI (0.6 mg, 3 μmol) in 2 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk flask, degassed and stirred under N_2 for 5 min at room temperature. The ethynyl derivative **8c** (117 mg, 1.00 mmol) was added; the reaction was then

sealed and stirred at room temperature overnight. Methanol was added to precipitate the polymer which was then filtered off and washed several times with methanol to give a yellow solid (82 mg, 89%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.6-1.0 (br m, 3nH); 1-1.6 (br m, 18nH); 1.6-2.0 (br m, 2nH); 3.4-4.2 (br m, 4nH); 6.4-7.7 (m, 18nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 158.8; 146.6; 137.5; 133.0; 131.8; 129.9; 128.2; 126.8; 123.7; 122.5; 114.7; 112.5; 96.1; 90.0; 86.4; 68.2; 32.2; 29.8; 29.5; 26.3; 22.9; 14.4.

IR (cm^{-1}): 3475, 3382, 3209, 3031, 2923, 2850, 2202, 1604, 1512, 1288, 1249, 1172, 960, 817.8, 524.

Elem. Anal. C, 84.95%; H, 6.92%; N, 2.14%; I, 0.2% (calc. for complete reaction C, 87.23%; H, 7.82%; N, 2.31%; I, 0.00%). The low carbon value is quite typical for high carbon materials. Such effects have been observed in most cases of PPEs and relatives.

Polymer 9a: Same procedure as **9c**, using **8a** (98 mg, 1.0 mmol) as ethynyl derivative. (85 mg, 97%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.1-0.5 (br m, 9nH); 0.75-0.95 (br m, 3nH); 0.95-1.55 (br m, 18nH); 1.7-2.1 (br m, 2nH); 3.8-4.2 (br m, 2nH); 6.0-8.5 (br m, 14nH).

IR (cm^{-1}): 3031, 2923, 2854, 2202, 2148, 1604, 1512, 1249, 1172, 960, 817, 759, 528.

Elem. Anal. C, 77.6%; H, 7.1%; I, 0.8% (calc. for complete reaction C, 83.90%; H, 8.59%; I, 0.00%) The low carbon value is quite typical for high carbon materials. Such effects have been observed in most cases of PPEs and relatives.

Polymer 9b: Same procedure as **9c**, using **8b** (102 mg, 1.00 mmol) as ethynyl derivative. (77 mg, 88%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.0-8.5 (br m, 19nH).

IR (cm^{-1}): 3031, 2923, 2850, 2202, 1604, 1512, 1249, 1172, 956, 813, 752, 524.

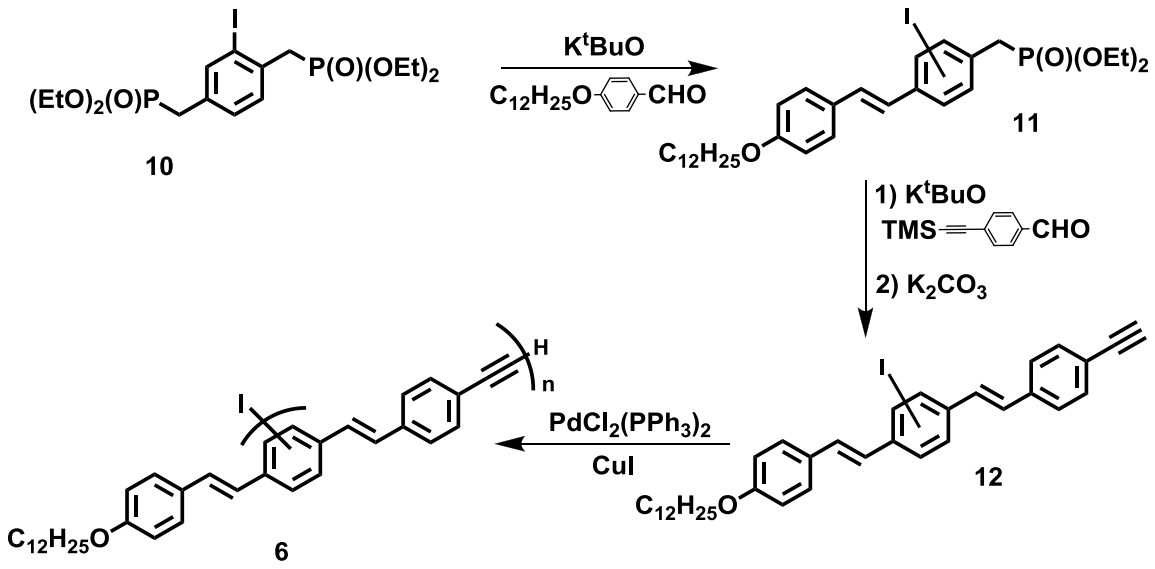
Elem. Anal. C, 85.03%; H, 6.44%; I, 0.2% (calc. for complete reaction C, 89.44%; H, 7.85%; I, 0.00%). The low carbon value is quite typical for high carbon materials. Such effects have been observed in most cases of PPEs and relatives.

Polymer 9d: Same procedure as **9c**, using **8d** (230 mg, 1.00 mmol) as ethynyl derivative. (91 mg, 85%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.70-1.05 (br m, 9nH); 1.05-1.50 (br m, 22nH); 1.50-1.70 (br m, 4nH); 1.70-1.90 (br m, 2nH); 3.0-3.5 (br m, 4nH); 3.6-4.2 (br m, 2nH); 6.0-8.5 (br m, 18nH)

IR (cm^{-1}): 3406, 3031, 2923, 2854, 2194, 1604, 1515, 1249, 1172, 960, 813, 524.

Elem. Anal. C, 84.66%; H, 7.34%; N, 2.02%; I, 0.3% (calc. for complete reaction C, 86.98%; H, 8.84%; N, 1.95%; I, 0.00%) The low carbon value is quite typical for high carbon materials. Such effects have been observed in most cases of PPEs and relatives.



Scheme 2.5. Synthesis of 6.

Asymmetric Monophosphonate 11: General procedure A was employed using compound **10** as starting material (2.31 g, 4.58 mmol). The crude mixture was purified by column chromatography (hexanes / ethyl acetate 3:2) to provide the mixture of isomers as colorless solid. (830 mg, 35%)

Mp: 65.0-68.5 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.88 (t, 6H, *J* = 6Hz); 1.24-1.40 (m, 44H); 1.40-1.52 (m, 4H); 1.74-1.86 (m, 4H); 3.08 (d, 2H, *J* = 22 Hz); 3.32 (d, 2H, *J* = 22 Hz); 3.90-4.14 (m, 12H); 6.82 (d, 1H, *J* = 16 Hz); 6.87-6.92 (m, 5H); 7.02 (d, 1H, *J* = 16 Hz); 7.14 (d, 1H, *J* = 16 Hz); 7.26-7.30 (m, 1H); 7.40-7.43 (m, 4H); 7.46 (d, 2H, *J* = 9 Hz); 7.53 (d, 1H, *J* = 8 Hz); 7.78 (t, 1H, *J* =2 Hz); 7.95 (s, 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.4; 140.8 (d, *J* = 7 Hz); 139.4 (d, *J* = 4 Hz); 138.6 (d, *J* = 4 Hz); 137.4 (d, *J* = 3 Hz); 134.1 (d, *J* = 9 Hz); 132.5 (d, *J* = 9 Hz); 131.3; 130.8 (d, *J* = 6 Hz); 130.1 (d, *J* = 6 Hz); 129.7; 129.6; 128.1; 126.3 (d, *J* = 3 Hz); 125.9 (d, *J* = 3 Hz); 124.3; 115.0;

101.9 (d, *J* = 10 Hz); 100.4 (d, *J* = 4 Hz); 68.3; 62.6 (d, *J* =7 Hz); 38.4 (d, *J* = 137 Hz); 32.9 (d, *J* = 137 Hz); 32.2; 29.9; 29.9; 29.8; 29.8; 296; 29.6; 29.5; 26.3; 22.9; 16.7 (d, *J* =6 Hz); 14.4.

IR (cm^{-1}): 3039, 2981, 2920, 2846, 2044, 1735, 1608, 1508, 1473, 1392, 1245, 1026, 794, 570.9.

Asymmetric Monomer 12: General procedure B was employed, using the isomeric mixture of **11** as starting material (585 mg, 0.913 mmol). The crude mixture was purified by column chromatography (hexanes / dichloromethane 9:1) to provide the mixture of isomers as yellow solid. (380 mg, 67%)

Mp: 80.0-84.0ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.88 (t, 6H, *J* = 6 Hz); 1.24-1.40 (m, 32H); 1.40-1.52 (m, 4H); 1.74-1.86 (m, 4H); 3.14 (s, 1H); 3.15 (s, 1H); 3.98 (t, 4H, *J* = 7 Hz); 6.82-7.09 (m, 10H); 7.18 (d, 1H, *J* = 16 Hz); 7.34 (d, 1H, *J* = 16 Hz); 7.42-7.51 (m, 14H); 7.59 (d, 2H, *J* = 8 Hz); 7.99 (d, 1H, *J* = 1 Hz); 8.01 (d, 1H, *J* = 2 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.5; 140.0; 139.3; 138.4; 137.9; 137.7; 137.7; 137.5; 133.5; 132.8; 131.4; 130.3; 129.9; 129.6; 128.8; 128.4; 128.1; 126.9; 126.7; 126.7; 126.4; 126.3; 126.0; 124.3; 121.6; 115.0; 101.5; 101.1; 83.9; 78.4; 68.3; 31.2; 29.9; 29.8; 29.6; 29.6; 29.5; 26.3; 22.9; 14.4.

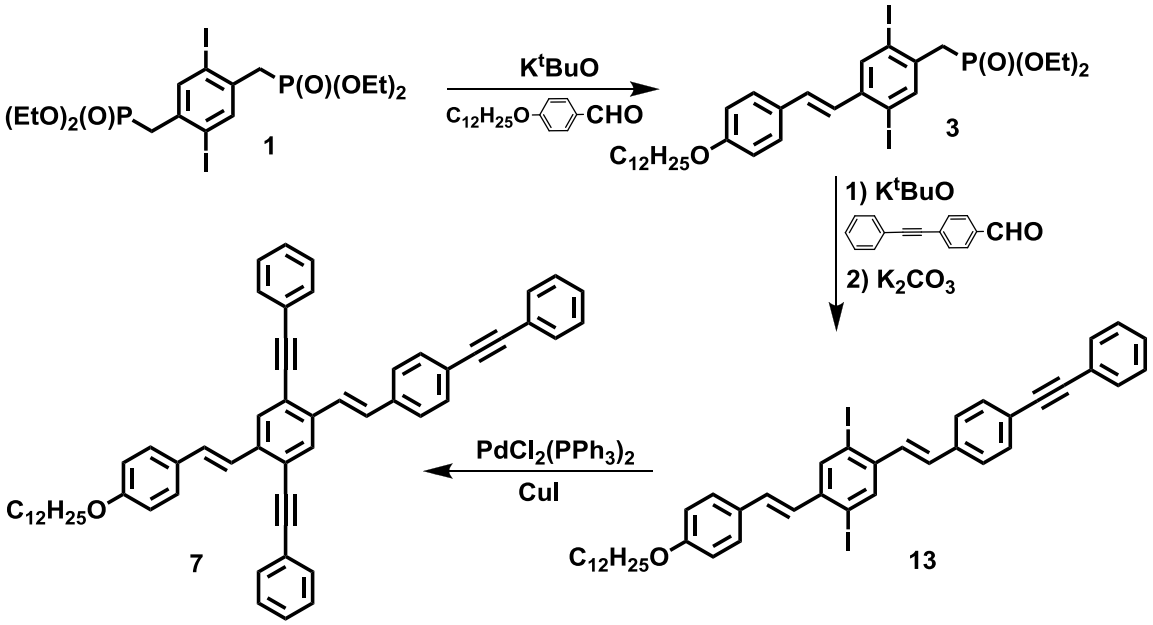
IR (cm^{-1}): 3267, 3031, 3004, 2920, 2846, 2098, 1604, 1512, 1469, 1450, 1284.5, 1245, 1176, 1029, 956, 852, 621.

MS (EI): (M^+) 616.3

Polymer 6: General procedure C was employed, using the isomeric mixture of monomers **12** as starting material (2.45 g, 3.82 mmol). Methanol was added to precipitate the polymer which was filtered off and washed several times with methanol to provide a yellow solid (1.53 g, 87%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.72-0.95 (br m, 3nH); 1-1.6 (br m, 18nH); 1.6-2 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.50-7.10 (br m, 3nH); 7.10-8.00 (br m, 12nH).

IR (cm^{-1}): 3028, 2923, 2850, 2202, 1604, 1512, 1249, 1172, 960, 825, 524.



Scheme 2.6. Synthesis of the XF model.

Asymmetric Monomer 13: General procedure B was employed, using **3** (1.23 g, 1.60 mmol) and 4-(phenylethynyl)benzaldehyde (330 mg, 1.62 mmol) as starting materials. The crude mixture was purified by column chromatography (hexanes / dichloromethane 9:1) to provide a yellow solid. (540 mg, 41%)

Mp: 145.5-147.5 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.88 (t, 3H, *J* = 6 Hz); 1.24-1.40 (m, 16H); 1.40-1.52 (m, 2H); 1.74-1.86 (m, 2H); 3.98 (t, 2H, *J* = 7 Hz); 6.88-7.02 (m, 5H); 7.20 (d, 1H, *J* = 16 Hz); 7.35-7.37

(m, 3H); 7.47 (d, 2H, *J* = 9 Hz); 7.51 (broad s, 4H); 7.55 (d, 2H, *J* = 4 Hz); 8.02 (s, 1H); 8.02 (s, 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.8; 140.5; 140.1; 136.7; 136.7; 136.7; 136.5; 136.2; 132.3; 132.2; 131.8; 131.5; 129.3; 128.6; 128.5; 128.2; 127.1; 123.5; 123.2; 115.0; 100.8; 100.5; 90.8; 89.7; 68.3; 32.2; 29.9; 29.7; 29.6; 29.5; 26.3; 23.0; 14.4

IR (cm^{-1}): 3035, 2916, 2850, 1604, 1512, 1469, 1249, 1041, 759, 520.

Compound 7: General procedure D was employed, using **13** (190 mg, 0.234 mmol) and phenylacetylene (204 mg, 1.99 mmol) as starting materials. The crude mixture was purified by column chromatography (hexanes / dichloromethane 9:1) to provide a yellow solid. (107 mg, 60%)

Mp: 196.0-197.0 ºC

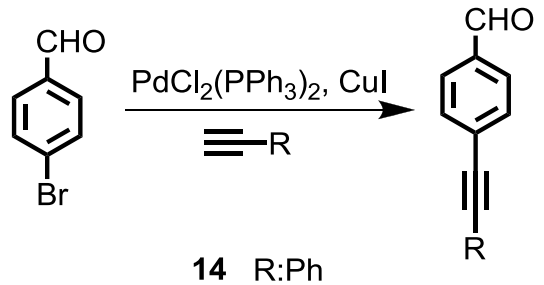
^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.88 (t, 3H, *J* = 6 Hz); 1.24-1.40 (m, 16H); 1.40-1.52 (m, 2H); 1.74-1.86 (m, 2H); 3.98 (t, 2H, *J* = 7 Hz); 6.91 (d, 2H, *J* = 9 Hz); 7.18-7.25 (m, 2H); 7.35-7.45 (m, 9H); 7.45-7.64 (m, 13H); 7.68 (d, 1H, 16 Hz); 7.87 (s, 1H); 7.87 (s, 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.5; 138.2; 137.5; 136.8; 132.2; 131.8; 130.7; 130.0; 129.8; 129.1; 128.9; 128.8; 128.7; 128.6; 128.5; 128.3; 126.9; 126.8; 126.5; 123.4; 123.4; 122.8; 122.6; 122.2; 115.0; 95.8; 95.7; 90.8; 89.9; 88.2; 88.1; 68.3; 32.2; 29.9; 29.9; 29.9; 29.9; 29.7; 29.6; 29.5; 26.3; 23.0; 14.4.

IR (cm^{-1}): 3031, 2916, 2850, 1604, 1573, 1496, 1469, 1249, 1176, 960, 817, 756, 686, 520.

MS (EI): (M^+) 766.4

Elem. Anal. C, 89.32%; H, 6.0%; O, 1.7% (calc. C, 90.82%; H, 7.10%; O, 2.09%)



14 R:Ph

15 R:TMS

Scheme 2.7. Synthesis of aldehydes **14** and **15.**

Compound 14[6]**:** General procedure D was employed, using 4-bromobenzaldehyde (3.29 g, 17.8 mmol) and phenylacetylene (2.04 g, 19.8 mmol) as starting materials. The crude mixture was purified by column chromatography (hexanes / dichloromethane 3:2) providing a colorless solid. (3.16 g, 86%)

Mp: 96.5-98.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 7.54-7.38 (m, 3H); 7.54-7.57 (m, 2H); 7.66 (d, 2H, *J* = 8 Hz); 7.86 (d, 2H, *J* = 14 Hz); 10.00 (s, 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 191.7; 135.6; 132.3; 132.0; 129.8; 129.2; 128.7; 122.7; 93.7; 88.8.

IR (cm^{-1}): 3359, 3047, 2846, 2742, 2214, 1948, 1701, 1600, 1384, 1207, 813, 752.

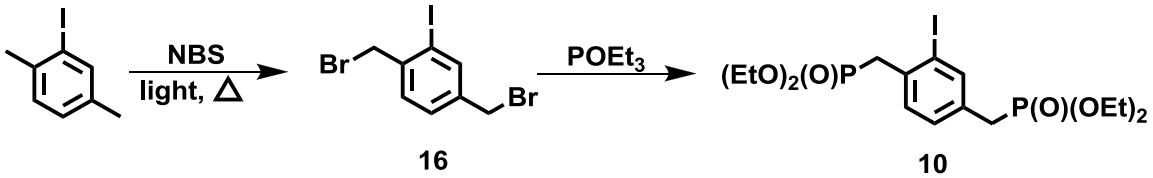
Compound 15[7]**:** General procedure D was employed, using bromobenzaldehyde (18.3 g, 0.102 mol) and trimethylsilylacetylene (10.9 g, 0.111 mol) as starting materials. The crude mixture was purified by column chromatography (hexanes / dichloromethane 3:2) to provide a colorless solid. (12.6 g, 63%)

Mp: 68.0-69.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.24 (s, 9H); 7.56 (d, 2H, *J* = 8 Hz) 7.87 (d, 2H, *J* = 8 Hz); 9.95 (s, 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 191.6; 135.7; 132.6; 129.6, 129.5; 104.1; 99.2; 0.0.

IR (cm^{-1}): 3803. 3718, 3652, 3379, 3058, 2958, 2896, 2831, 2738, 2156, 1701, 1600, 1380, 1207, 786, 532.



16 10

Scheme 2.8. Synthesis of compound 10.

Compound 16: 2-iodo-para-xylene (6.96 g, 30.2 mmol) and *N*-bromosuccinimide (11.8 g, 65.8 mmol) were placed in a round bottom flask and 200 mL of CH_3CN were added. The reaction was refluxed under the light of one 120 W sunlamp for 3 h. After this time, the mixture was allowed to cool to room temperature and decolorized with an aqueous solution of sodium sulfite. The organic phase was extracted three times with DCM (3 x 150 mL) and the combined organic layers were dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the crude mixture was purified by column chromatography (hexanes / dichloromethane 9:1) to provide a colorless solid. (1.67 g, 11%)

Mp: 112.0-113.5 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 4.37 (s, 1H); 4.55 (s, 1H); 7.36 (dd, 1H, *J* = 2 Hz, 8 Hz); 7.44 (d, 1H, *J* = 8 Hz); 7.88 (d, 1H, *J* = 2 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 140.3; 140.3; 139.7; 130.6; 129.5; 99.9; 38.0; 31.0.

IR (cm^{-1}): 3899, 3028, 2974, 2846, 2630, 2434, 2230, 1982, 1905, 1786, 1593, 1485, 1431, 1396, 1226, 1199, 894, 833, 632.

Compound 10: Compound **16** (5.50 g, 14.1 mmol) was dissolved in 25 mL of triethylphosphite and the mixture was stirred at 140 ºC for 4 h under reflux. Hexanes were added and the flask was left in the freezer until a transparent oil remained in a different phase, becoming a white solid afterwards. The precipitate was filtered and washed with hexanes to provide a colorless solid. (5.25 g, 74%)

Mp: 43.5-45.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 1.25 (t, 12H, *J* = 7 Hz), 3.05 (d, 2H, *J* = 20 Hz); 3.38 (d, 2H, *J* = 20 Hz); 4.02 (m, 8H); 7.25 (d, 1H, *J* = 8 Hz); 7.40 (m, 1H); 7.77 (s, 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz):140.8 (d, *J* = 6 Hz); 134.3 (dd, *J* = 4 Hz, 9 Hz); 132.6 (dd, *J* = 4 Hz, 9 Hz); 130.7 (dd, *J* = 3 Hz, 6 Hz); 130.0 (d, *J* = 3 Hz, 6 Hz); 101.3 (dd, *J* = 4 Hz, 9 Hz); 62.4 (dd, *J* = 3 Hz, 6 Hz); 38.1 (d, *J* = 138 Hz); 32.8 (d, *J* = 138 Hz); 16.3 (d, *J* = 6 Hz).

IR (cm^{-1}): 2977, 2908, 2441, 2264, 2191, 1917, 1778, 1747, 1596, 1485, 1388, 1226, 1053, 848, 590

2.3.3 Supplemental Data

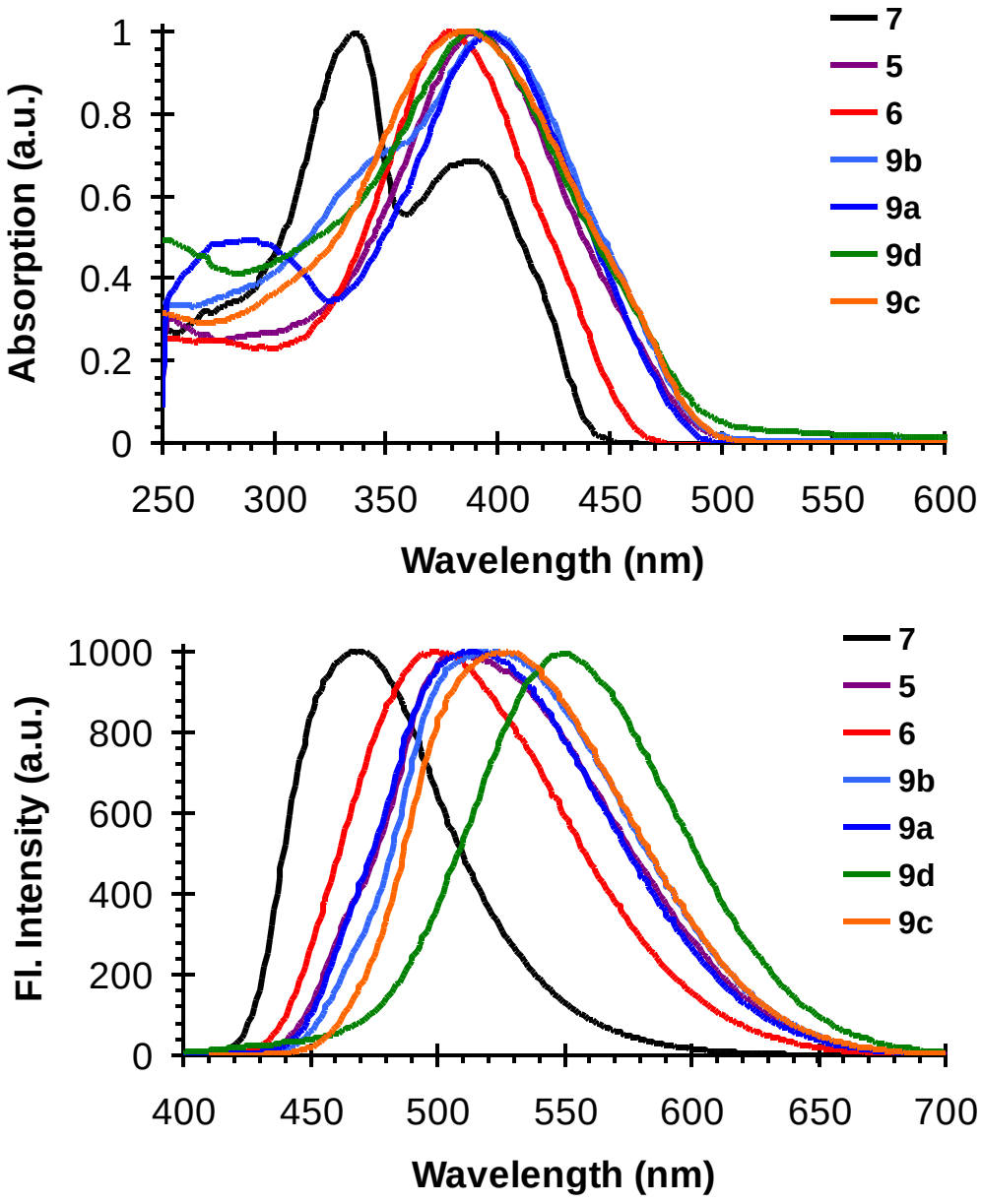
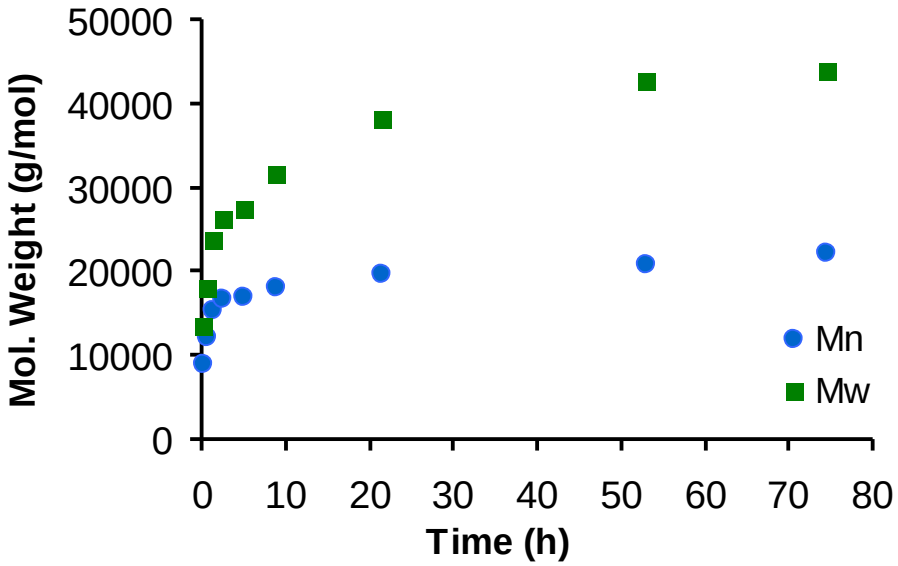


Figure 2.3. Normalized absorption (top) and emission (bottom) spectra of 5 x 10^{-6} M solutions of XF **7** and polymers **5**, **6** and **9a-d** in DCM.



	1	2	3	4	5	6	7	8	9
time (h)	0.33	0.75	1.42	2.5	5	9	21.42	52.92	74.42
Mn	8885	12154	15232	16698	16785	18067	19724	20798	22224
Mw	13487	18117	23767	26145	27348	31589	38217	42615	43850
Mz	46288	36277	47409	48152	53147	65526	86722	93408	86870
polyd. index	1.518	1.491	1.560	1.566	1.629	1.748	1.938	2.001	1.884

Figure 2.4. Evolution of hyperbranched polymer **5** during polymerization.

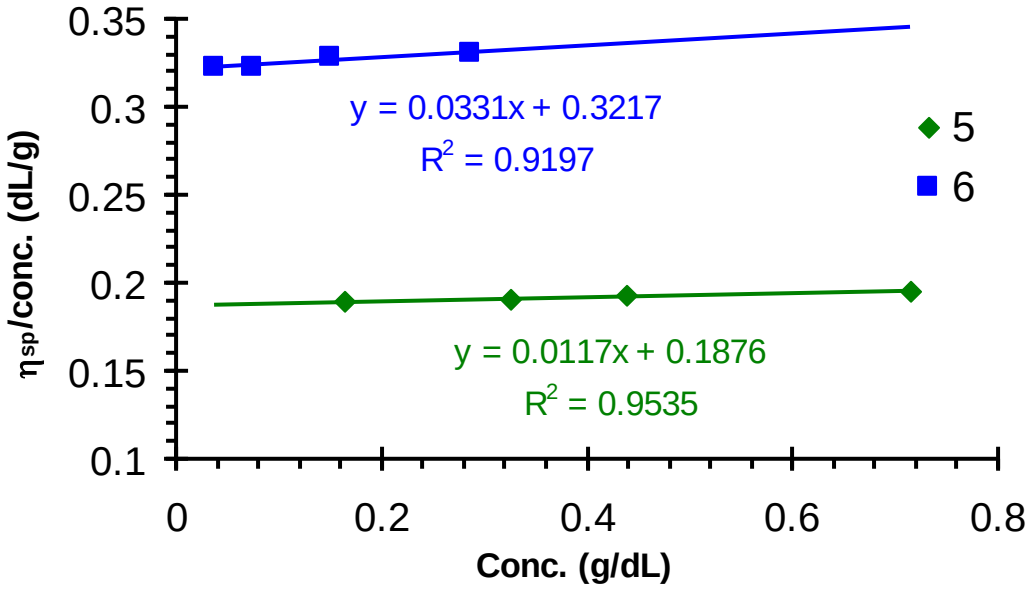


Figure 2.5. Huggins equation plot for hyperbranched polymer **5** (green) and linear polymer **6** (blue).

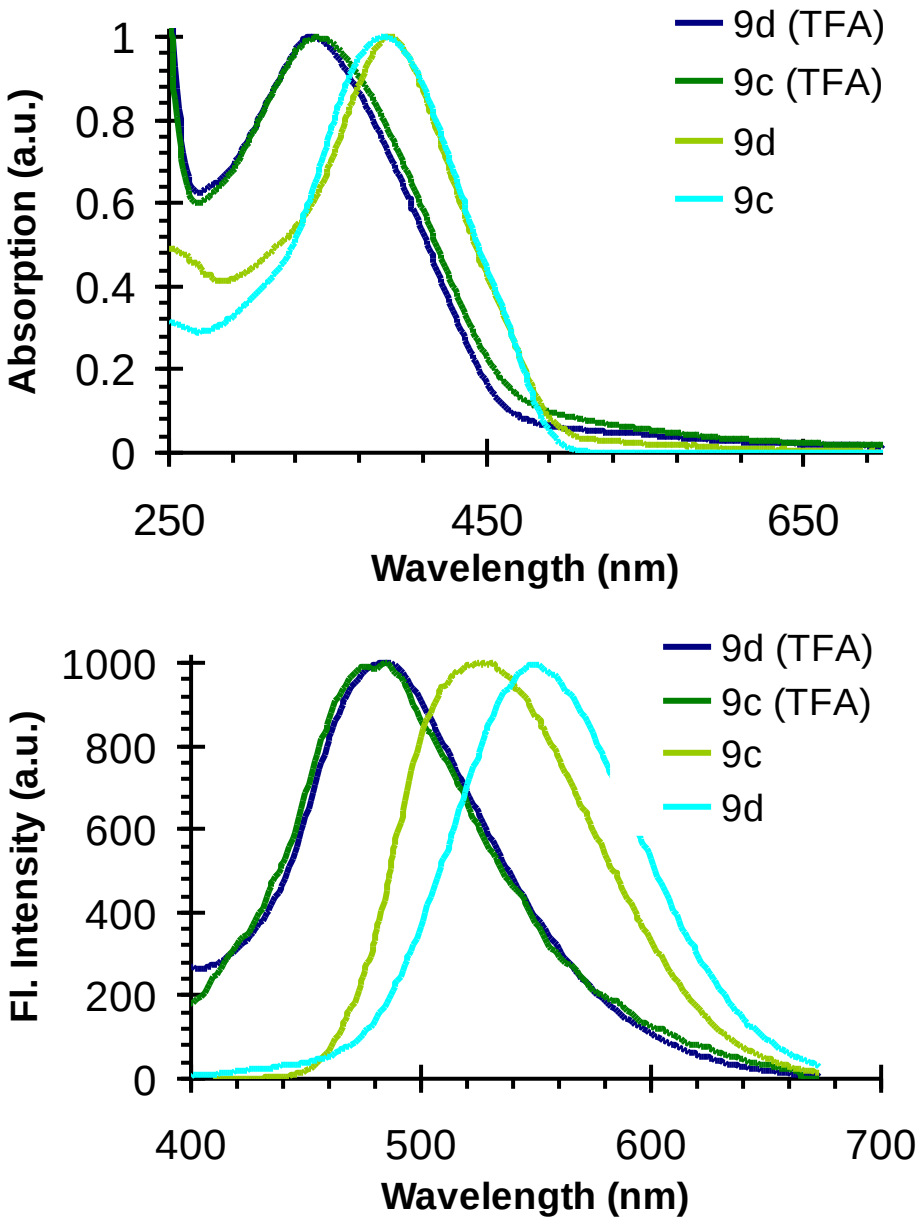


Figure 2.6. Normalized absorption (top) and emission (bottom) spectra of 5 x 10^{-6} M solutions in DCM of polymers **9c** and **9d** in presence and absence of an excess of TFA.

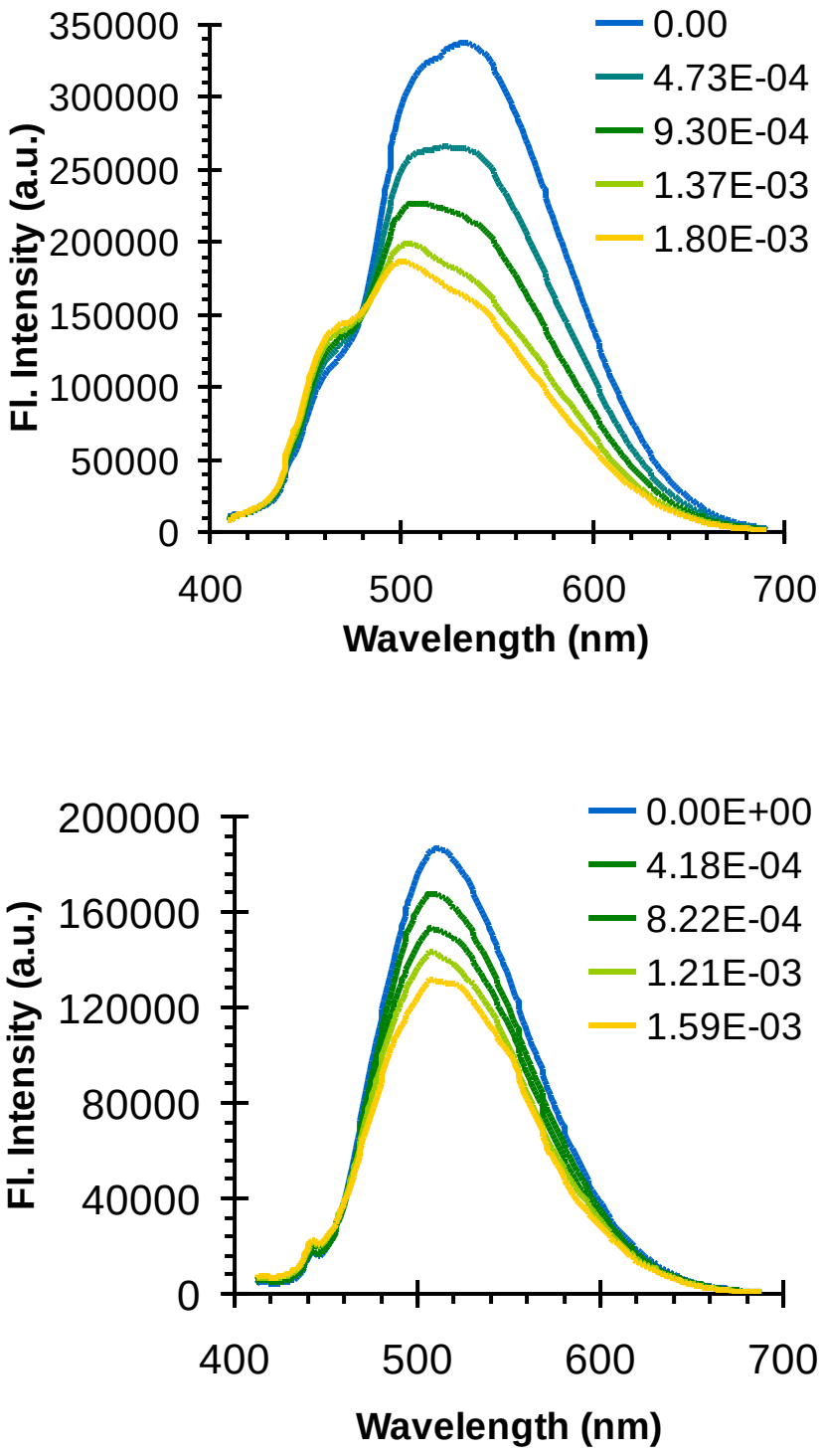


Figure 2.7. Normalized emission spectra of 7.7 x 10^{-6} M solutions in THF/methanol (1:2) of polymers **9b** (top) and **6** (bottom) in the presence of given concentrations (legend, in mol/L) of paraquat.

2.4 References

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CHAPTER 3

POSTFUNCTIONALIZATION OF HYPERBRANCHED CONJUGATED POLYMERS

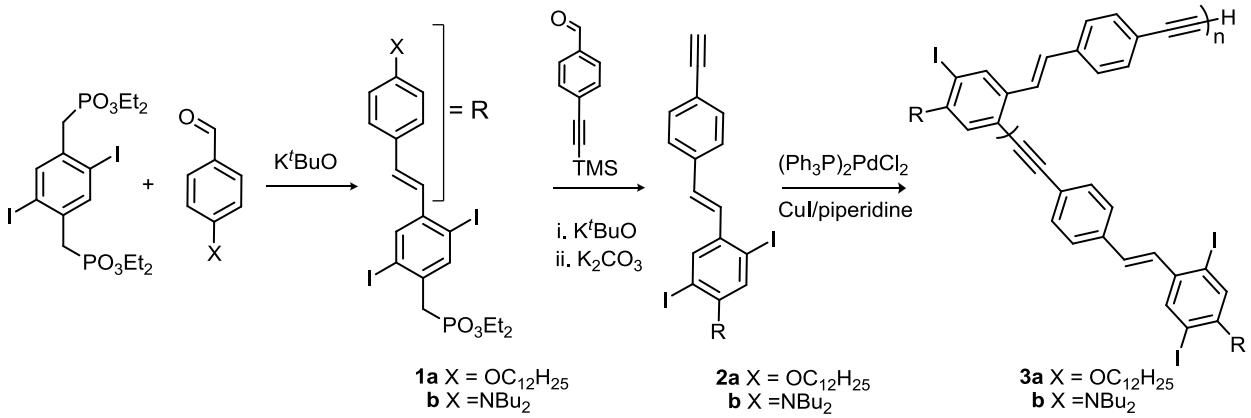
3.1 Abstract

This chapter continues the discussion hyperbranched poly(phenylene vinylene-phenylene ethynylene) scaffolds, focusing on their postfunctionalization. It studies the hyperbranched dodecyloxy-substituted polymer described in Chapter 2, but also a hyperbranched dibutylamino-substituted polymer, a polymer with a stronger electron-donating group. Both hyperbranched polymer scaffolds are functionalized extensively, providing 24 derivatives that are substituted to near completion. The absorbance, emission and quantum yields of the derivatives are studied in solution, and absorbance and emission are studied in solid state, both studies showing the strong effect of postfunctionalization on electronic structure. Protonation of the polymers is studied, showing the importance of the position and distribution of electron-donating dibutylamino groups in the optical properties of the polymers.

3.2 Results and Discussion

Scheme 3.1 displays the synthesis of polymers **3a** and **3b**. Following the same approach used for the preparation of asymmetric cruciforms,[1] monomers **2a** and **2b** were constructed by monoalkenylation of the diphosphonate to furnish **1a** and **1b** in acceptable yields. After a second Horner reaction with 4-(trimethylsilylethynyl)benzaldehyde and subsequent deprotection with potassium carbonate, the desired monomers **2a** and **2b** were obtained. Sonogashira polymerization of **2a** and **2b** leads to the hyperbranched polymers **3a** and **3b** in 87 and 81% yield, respectively. These hyperbranched polymers are powdery orange solids soluble in

common organic solvents. Both show expectedly low quantum yields (0.014 and 0.004 respectively) in solution due to the heavy atom effect of the iodine groups present in the polymeric skeleton. The molecular weight of **3a** is 2.4 x 10^4 g/mol with a polydispersity index M_w/M_n of 2.0 according to gel permeation chromatography (GPC). GPC measurements of **3b** show only peaks assigned to aggregated species, given how quickly they run off the column. An attempt was made to disrupt the aggregation of the polymer **3b** by catalytic hydrogenation of the conjugated structure,[2] but again, only signals due to aggregated polymers were recorded. The incorporation of *N*,*N*-dialkylanilines into the structure seems to induce the aggregation of the polymer inside the column, hampering an accurate measurement of their molecular weight. Despite the lack of a measurement of the molecular weight of **3b**, the ^{1}H NMR spectra of **3a** and **3b** show broad signals compared with those of the corresponding monomers **2a** and **2b** (Figure 3.1), suggesting polymerization of **3b**. Polymers **3a** and **3b** contain one iodine substituent per repeat unit, however, different from linear or truly dendritic polymers, these iodine groups are statistically distributed over terminal and linear modules in the formed hyperbranched polymers. The donor character of the amino groups in **3b** destabilizes its highest occupied molecular orbital. As a result, a strong bathochromic effect compared with **3a** is observed in its absorption and fluorescent response (Figure 3.2).



Scheme 3.1. Synthesis of hyperbranched iodinated polymers by Pd-catalyzed coupling.

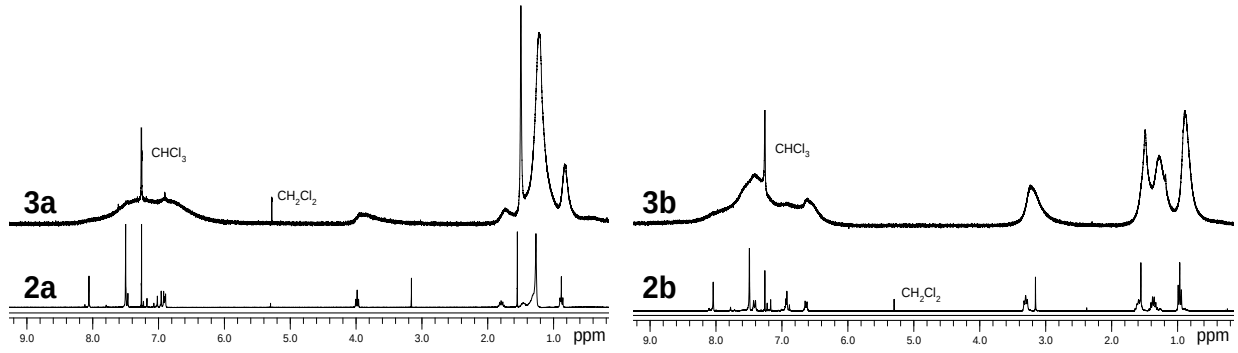


Figure 3.1. ^{1}H NMR spectra of monomers **2a** and **2b** (bottom) and polymers **3a** and **3b** prepared from them (top). Broad signals in **3a** and **3b** indicate a similar degree of polymerization.

A library of hyperbranched polymers **5** and **6** was obtained by coupling **3a** and **3b** to the alkynes **4a-t** (Scheme 3.2) using Sonogashira conditions. The set of alkynes **4a-t** includes donor and acceptor species with different heteroatoms, aliphatic and aromatic substituents, heterocycles and complex structures such as **4r**, a T-shaped alkyne featuring two dibutylamino groups; or **4t**, a flavin derivative potentially useful in supramolecular chemistry.[3] All reactions were followed by a simple work-up consisting of the precipitation of the polymers into methanol. The yields are generally above 85%, with all products isolated as yellow to red powders (**5a-t** from **3a**, and **6a-q** from **3b**). In most cases, NMR spectroscopy was not very useful to elucidate the functionalization of the polymer, due to the broad signals in the aromatic region of the spectrum.

Therefore, combustion analyses were performed to assess the remaining amount of iodine present in the polymer after the reaction and to have a handle on the degree of the postfunctionalization (Table 3.1). In all cases but **5n** and **5f**, the iodine content is lower than 1%. These values indicate that more than 95% of iodine groups have been replaced by the corresponding alkyne. A graphic of the average number molecular weight of the new polymers, as measured by gel permeation chromatography (GPC), compared with their theoretical values if complete substitution of the iodines in **3a** is assumed, also confirms the high degree of functionalization (Figure 3.3). A linear regression of these values shows a gradient (Mn_{exp}/Mn_{th}) near to the expected 1 (y = 1.1x).

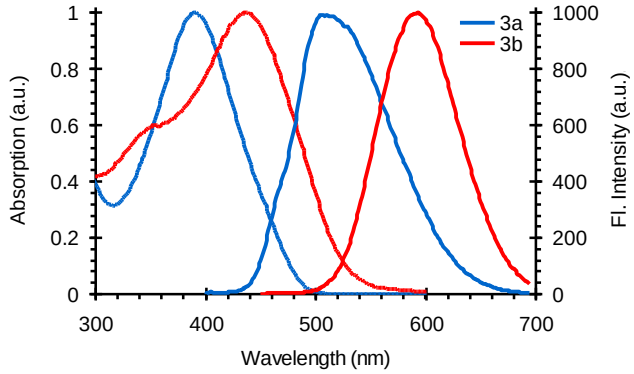


Figure 3.2. Normalized absorption and emission of solutions of **3a** and **3b** in dichloromethane.

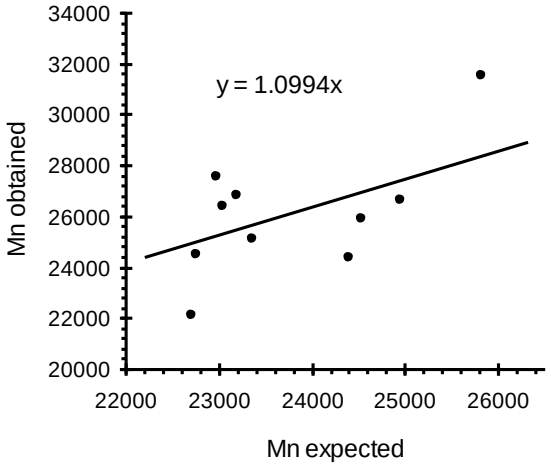
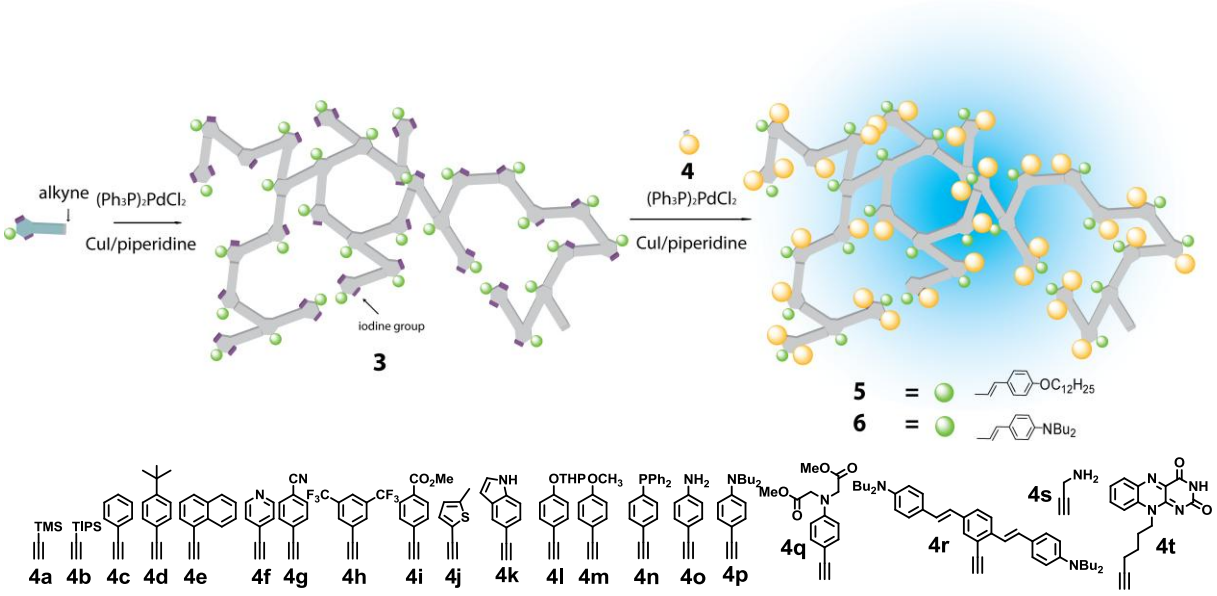


Figure 3.3. Average number molecular weight by GPC and theoretical molecular weight average number in postfunctionalization reactions for derivatives of **5**.



Scheme 3.2. Postfunctionalization of the hyperbranched polymer **3** by Pd-catalyzed couplings to different alkynes **4.**

To elucidate the effect of the substituents on the electronic properties of polymers, UV-vis and emission spectra in solution and in the solid state were recorded. Figure 3.4 displays photographs of solutions of the polymers **5** and **6** in dichloromethane as well as a selection of them in their solid state. The pictures were taken under black light illumination at λ_{em} = 366 nm. Qualitatively, the observed emission of the polymers varies from blue-green for **5a** to orange-red for **6h**. The strong solid-state emission of the polymers shows bathochromically shifted features compared to their spectra in solution, ranging from yellow (**5l**) to red (**6h**), depending on the substitution. The principal spectroscopic properties of **3a-b** and the postfunctionalized polymers **5a-t** and **6a-q** are shown in Table 3.1. Without much changes in the absorption spectra, the incorporation of different functional groups into the polymeric structure leads to a general increase of the quantum yields up to a factor of 20, as a consequence of the removal of the iodine groups. The derivatives **5f**, **5r** and **5t** are exceptions to this behavior. The presence of pyridinic

nitrogen leads to an almost quenched emission in **5f** and **5t**. The fluorescence of **5r** in dichloromethane shows a dual emission with main band centered at 515 nm and a shoulder around 595 nm corresponding to **4r** (Figure 3.5). The emissive lifetime of the two bands are significantly different (τ_{515} = 1.2 ns and τ_{595} = 2.0 ns).[4] According to the longest lifetime of the red-shifted band, an inefficient energy transfer from the polymeric backbone to the bis(dibutylaminostyryl) moiety in solution is postulated to explain the low quantum yields of **5r**. The energy transfer is more efficient in the solid state and this secondary band appears to be the only one observed in solid state (λ_{max} = 612 nm). It is notable from Figure 3.4 that **5r** is brightly fluorescent in solid state but almost non-fluorescent in solution reinforcing our assumption of the efficient energy transfer.

From **5a** to **5e**, an extension of the conjugation causes a red-shift of the fluorescence. Naphthyl-substituted **5e** is slightly bathochromically shifted from the indole substituted polymer **5k**. The presence of electron-withdrawing groups also induces a red-shift, as is observed in **5g-i** and especially in **6h**, a donor-acceptor system, which shows an emission maximum at 602 nm. Electron donating substituents in the polymers prepared from **3a** experience a red-shift of the fluorescence. On the other hand, no significant effect is observed in those prepared from **3b**, as a strong donor is already present in the structure. Polymer **5p** shows the strongest bathochromic effect upon the emission in solution, whereas **5r** is the most red-shifted polymer of its family in the solid state. Sterics also have a significant influence on the fluorescence of the polymers; **6a** and **6b**, TMS and TIPS substituted polymers respectively, show a different fluorescent response both in solution and solid state. In the solid state, the bulkier substituent in **6b** increases the quantum yield and induces a blue-shift in fluorescence compared to **6a**. This behavior is surprisingly not observed for **5b** and **5a**.

Table 3.1. Chemical and Spectroscopic Data of Polymers **5** and **6**

	λ_{max} Absorption	λ_{max} Emission (nm)	Φ[%][c]	ε (L cm^{-1} mol^{-1})	Yield [%]	% iodo
3a	392	510 (553)[b]	1.4	84000	-	17.5
5a	397	513 (558)	24	43600	97	0.8
5b	397	513 (557)	25	58400	59	0.1
5c	397	522 (565)	11	32000	84	0.2
5d	397	523 (560)	13	42600	95	0.4
5e	375	533 (570)	15	59000	95	0.1
5f	396	505	2.1	51600	62	1.8
5g	395	519 (578)	7.2	45000	90	0.2
5h	396	527 (582)	10	54200	52	0.5
5i	395	528 (568)	16	44500	77	0.3
5j	395	523 (571)	14	32300	51	0.1
5k	389	524 (559)	5.9	32300	89	1.1
5l	396	527 (562)	24	51900	86	0.1
5n	386	519 (560)	4.3	25400	90	3.8
5o	386	528 (565)	13	60700	89	0.2
5p	392	553 (569)	2.1	65600	85	0.3
5r	407	517, 595[d] (612)	0.7	N/A	83	0.1
5s	378	502 (581)	2.6	8400	88	0.7
5t	394	504 (559)	1.7	57200	70	N/A
3b	437	586 (613)	0.4	66200	-	21.8
6a	441	593 (605)	9.2	58700	88	0.3
6b	442	587 (597)	15	60200	93	0.2
6c	354, 442	593 (618)	6.0	64200	91	0.8
6h	357, 438	602 (629)	5.1	57900	98	0.4
6m	362, 440	593 (616)	8.9	66500	94	0.3
6q	382, 441	592 (622)	13	70100	71	0.3

[a] Fluorescence measurements were performed in dichloromethane solutions of the polymers.
[b] Wavelength of maximum emission of the polymers in the solid state in parenthesis
[c] Quinine sulfate was used as standard in quantum yield measurements
[d] **5r** presents a significant shoulder around 595 nm

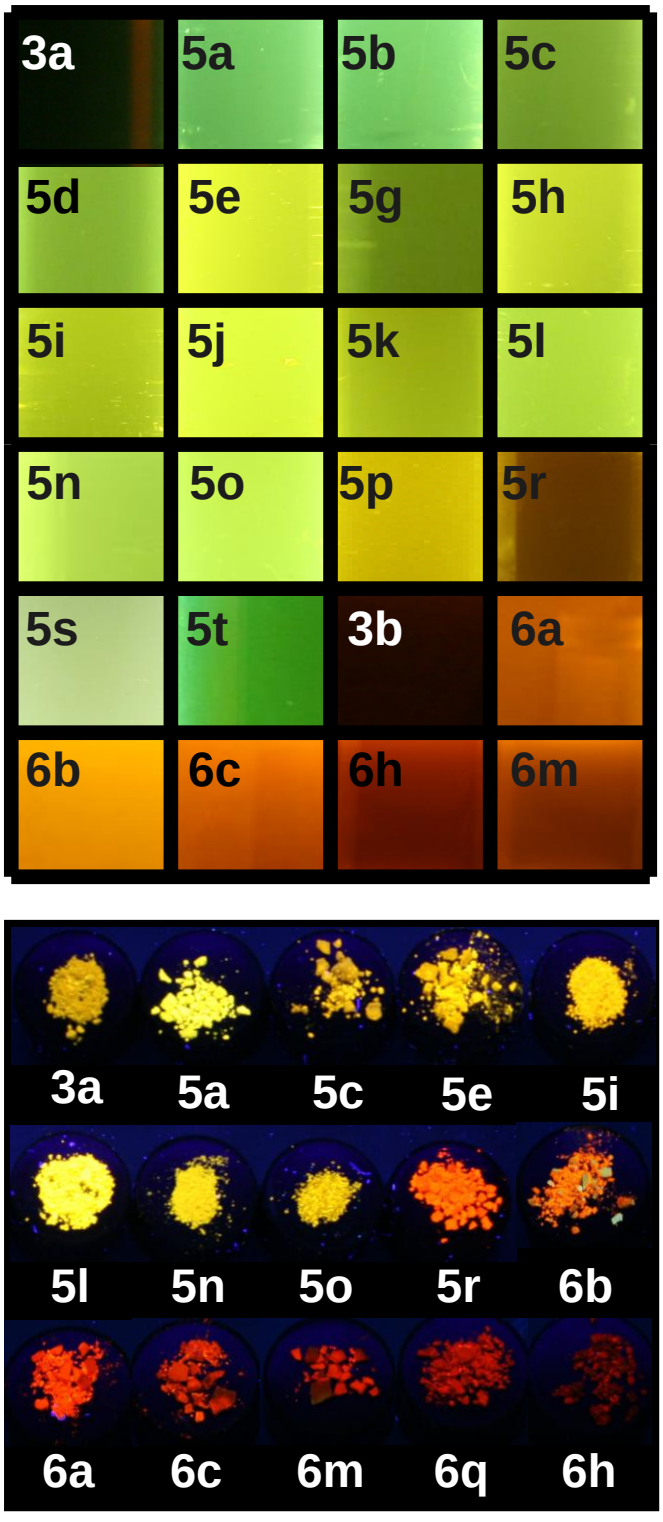


Figure 3.4. Photographs of fluorescent emission of polymers **5** and **6** in dichloromethane solutions (top) and in the solid state (bottom) under illumination using a hand-held blacklight (λ_{em} = 366 nm)

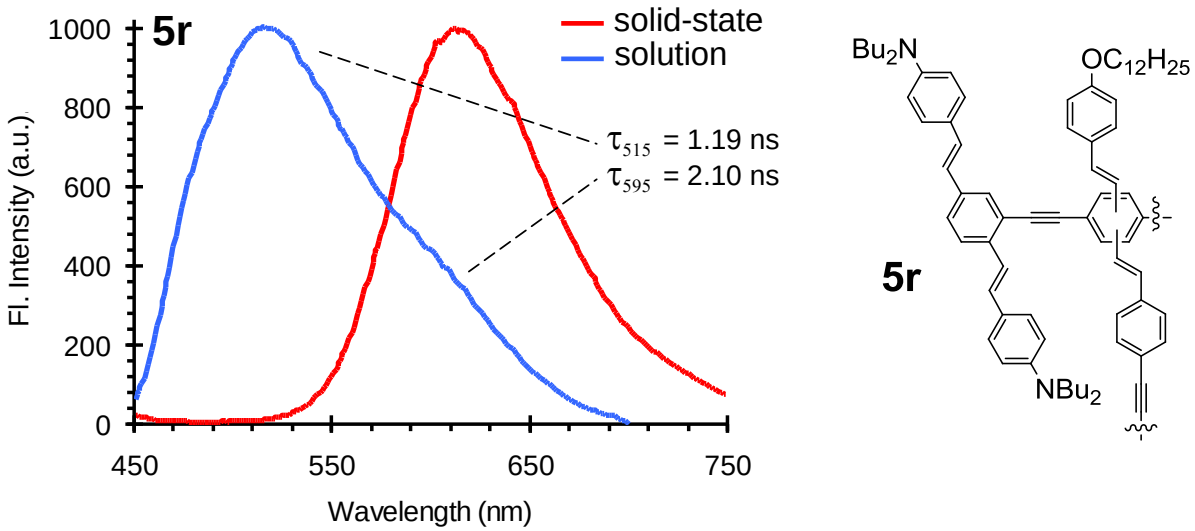


Figure 3.5. Emission spectra of **5r** in dichloromethane solution (blue) and in solid state (red). Fluorescence lifetimes of the two bands observed in the emission of **5r** in dichloromethane are presented.

In **5p** and **6m**, the pre- and postfunctional groups are similar but switched. The amino groups in **6m** seem to have a stronger influence on the electronic structure of the polymer than in **5p**, with a significant red-shift in both absorption (48 nm) and emission (40 nm) of **6m** compared to **5p**. The difference in the spectroscopic properties of **6m** and **5p** might be due to the difference in connection of the dialkylamino functionalities to the conjugated backbone. A recent study of the electronic characteristics of substituted distyrylbenzenes and bisarylethynylbenzenes reveals a general red-shift of the fluorescence of distyrylbenzene derivatives compared to their corresponding bisarylethynylbenzene pairs, due to the vinylic connection.[5] However, the significant change observed in the fluorescence of **6m** and **5p** has not been recorded in small molecules; as a consequence, it can be assumed that other factors might play a role. An examination of the polymer structure shows that in **6m** the dialkylamino groups are present in each monomeric unit of the polymer, while in **5p** the amines are located only where there were iodine groups in **3a**, that is, not necessarily on each monomer, since the position of the iodine

groups depends on the degree of branching of the hyperbranched polymers (Figure 3.6). Only in an ideal linear polymer will every monomeric unit contain an amine, while in a purely dendritic system only the peripheral units will carry two iodine substituents each. If the theoretical 50% degree of branching calculated for this type of monomer by Frechet et al. is assumed,[6] the number of amino groups situated in the inner part of the backbone will be much lower in **5p** than in **6m**. This difference in the distribution of amino groups might play a critical role in the different optical gaps of these two pseudoisomeric polymers.

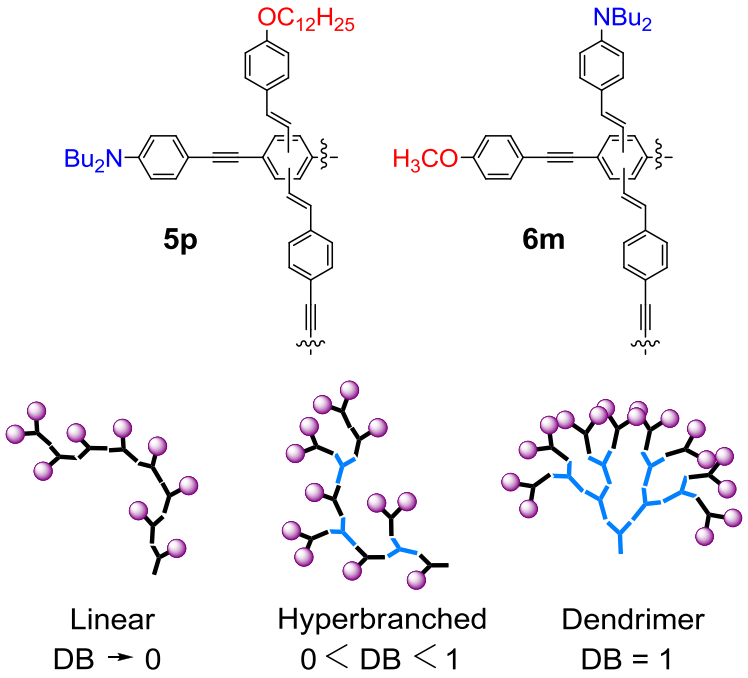


Figure 3.6. Simplified representation of the pseudo-isomers **5p** and **6m** showing the different connectivities of the functional groups to the polymer (top). Schematic view of the distribution of the alkynes after postfunctionalization (purple spheres) depending on the degree of branching (DB). Branching units (blue) do not bear postfunctional groups (bottom).

An attempt was made to confer water solubility to **5** by hydrolysis of **5i** to the corresponding carboxylate, and by the deprotection of the phenol group from **5l**. Although the results are promising, and both **5i** and **5l** dissolve in mixtures of methanol/water and THF/water,

they are not completely soluble in water. In the future alkynes that carry more than one carboxylate group will be used to imbue water solubility to these polymers.

As the frontier molecular orbitals of the polymer are influenced by electron pairs such as those in dialkylamino groups, their optical properties should vary upon metal complexation or protonation. To explore this response, the effect of protonation upon the photophysics of **5f**, **5n**, **5o**, **5p**, **5r** and **5t** as well as upon **6a-q** was examined. The results are shown in Table 3.2 (all spectra are presented in the 3.3 Experimental section). Upon addition of an excess of trifluoroacetic acid (TFA) to solutions of the polymers in dichloromethane, a strong blue-shift in the absorption is observed for the dialkylamino substituted polymers as well as for the triphenylphosphine substitued derivative **5n.** These shifts are mirrored in their emission spectra, where hypsochromic shifts are also measured upon protonation. These shifts are significant in **6a-q** (the polymers prepared from **3b)** and are accompanied by a large increase of their quantum yields. Polymers **5p** and **5r** also experience a modest increase of their quantum yields upon protonation of their amino groups. It is important to note that all of the emission maxima of the protonated species of the dialkylamino containing polymers converge at around 495-500 nm regardless of the relative position of the amino group in the polymer (Figure 3.7). Since the electron pairs of the amino groups are no longer available, the flourescence comes from the "naked" conjugated backbone. In the case of **5f** and **5t**, pyridine and flavin substitued derivatives respectively, the effect of protonation are almost imperceptible in absorption. Regarding the fluorescence, quenching of **5f** is observed while **5t** does not experience any change in either emission wavelength or quantum yields.

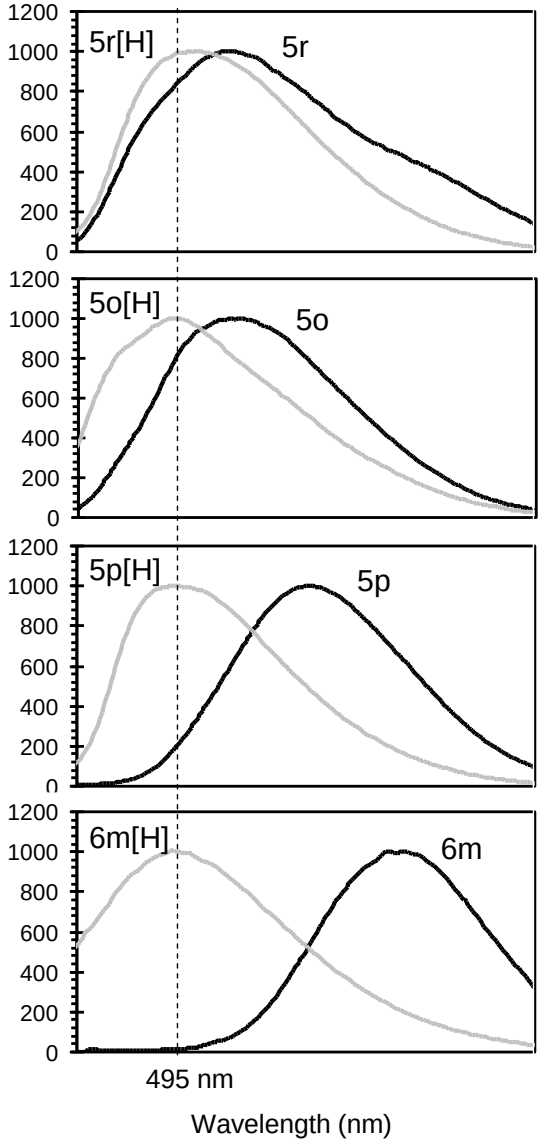


Figure 3.7. Selected fluorescent emission of some of the dialkylamino containing polymers (**5o**, **5p**, **5r** and **6m)** in dichloromethane (black traces) and upon addition of TFA (grey traces).

Table 3.2. Absorption and Emission of the polymers upon addition of TFA in dichloromethane

	λ_{max} Absorption	λ_{max} Emission (nm)	*Φ[%]*
5f	396 / 396	505 / quench	2.1 / quench
5n	386 / 355	519 / 498	4.3 / 0.9
5o	386 / 395	528 / 494	13 / 0.4
5p	392 / 358	553 / 494	2.1 / 5.8
5r	407 / 368	595 / 499	0.7 / 10.8
5t	394 / 389	504 / 501	1.7 / 0.5
6a	441 / 388	593 / 498	9.2 / 62
6b	442 / 384	587 / 485	15 / 66
6c	442 / 388	593 / 496	6.0 / 32
6h	438 / 388	602 / 495	5.1 / 28
6m	440 / 386	593 / 498	8.9 / 66
6q	441 / 378	592 / 510	13 / 19

[a] The values on the right correspond to the protonated species

3.3 Experimental

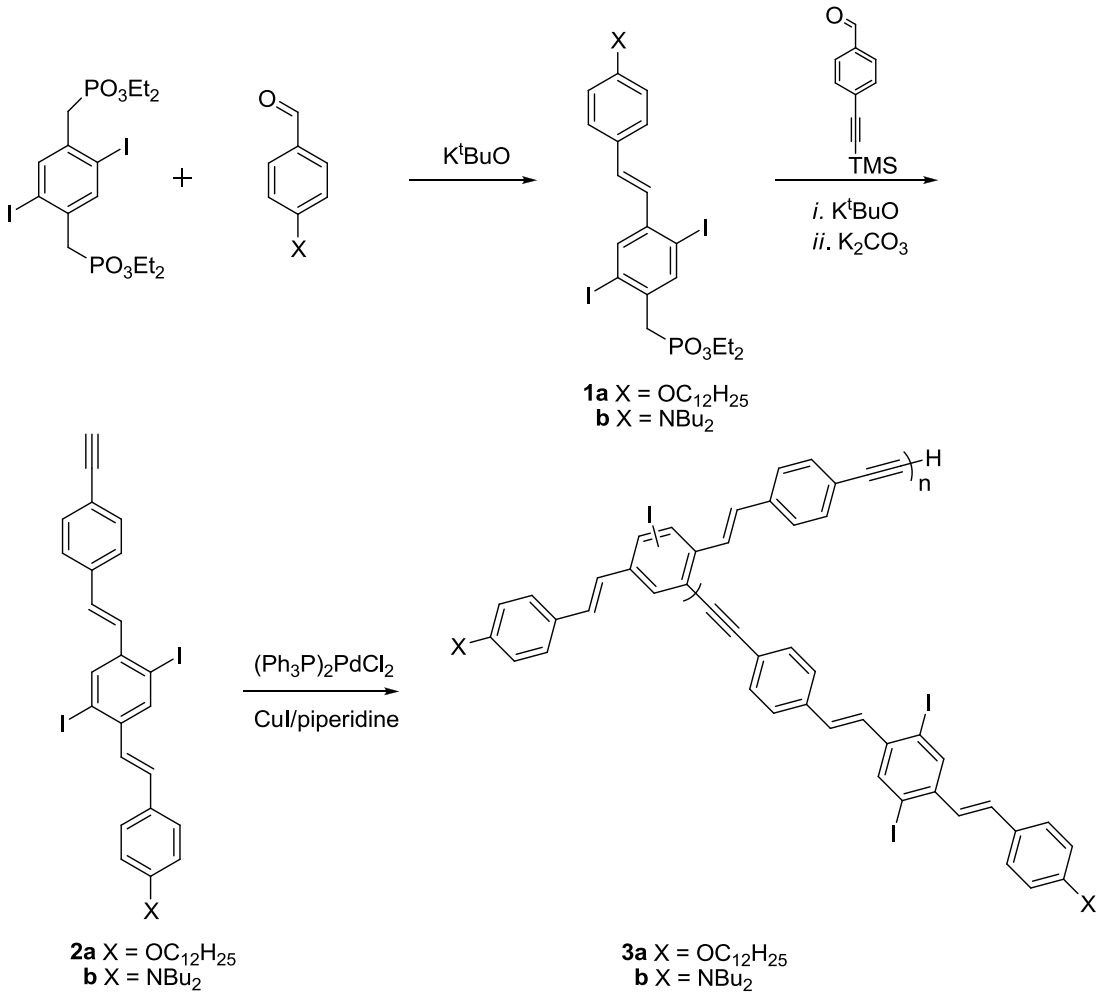
3.3.1 Materials and Methods.

All chemicals were purchased from Aldrich Chemical, Acros, TCI America, or Fischer Scientific and used without purification unless otherwise specified. Column chromatography was performed using Standard Grade silica gel 60 Å, 32-63 μm (230 x 450 mesh) from Sorbent Technologies and the indicated eluent. Elution of conjugated compounds was readily monitored using a handheld UV lamp (365 nm). Melting points were obtained using a Mel-Temp apparatus fitted with a Fluke 51K/J digital thermometer. All IR spectra were obtained using a Shimadzu FTIR-8400s spectrometer. Unless otherwise specified, NMR spectra were recorded at 298 K on a Varian Mercury spectrometer (300 MHz). Chemical shifts are reported in parts per million (ppm), using residual solvent (chloroform-*d*) as an internal standard (δ = 7.26 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, and integration. Mass spectral analyses were provided by the

Georgia Institute of Technology Mass Spectrometry Facility. GPC experiments were performed using a Shimadzu LC-10AT chromatographer with polystyrene standards for the molecular weights. Elemental analysis of the compounds was provided by Columbia Analytical Services.

All absorption spectra were collected using a Shimadzu UV-2401PC spectrophotometer. All emission spectra were acquired using a PTI LPS-220B spectrofluorophotometer. Quantum yields for the models and polymers were measured using standard procedures. In all cases, quinine sulfate was used as a standard and all solutions were purged with nitrogen prior to measurement. Lifetime data were collected using a Lifespec-ps (Edinburgh Instruments), pulsed diode laser (PicoQuant, 372 nm excitation), and PMT detector (Hamamatsu). Data were fit to single exponential decay so as to optimize chi-squared values. Pictures of luminescent solutions were taken with a Canon EOS 30D.

3.3.2 Synthesis



Scheme 3.3. Synthesis of the hyperbranched polymers.

Monophosphonate 1a: A solution of diphosphonate[7] (6.67 g, 10.7 mmol) in dry THF (100 mL) was stirred at 0ºC under N_2 while ^{t}BuOK (1.08 g, 9.67 mmol) was added carefully. After the addition, the reaction mixture was stirred for 3 min. Then, 4-dodecyloxybenzaldehyde (2.50 g, 8.59 mmol) in dry THF (15 mL) was added as quickly as possible. After 30-40 min, 100 mL of water, followed by 5 mL of a saturated solution of NH_4Cl, were added to quench the reaction. The mixture was extracted with DCM (3 x 100 mL). The combined organic phases were washed

with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the crude mixture was purified by column chromatography (ethyl acetate / hexane 1:2) to give **1a** as yellow solid. (2.75 g, 42%)

Mp: 56.5-58.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.88 (t, 3H, J = 6 Hz); 1.24-1.40 (m, 22H); 1.40-1.52 (m, 2H); 1.74-1.86 (m, 2H); 3.32 (d, 2H, *J* = 22 Hz); 3.97 (t, 2H, *J* = 12 Hz); 4.04-4.14 (m, 4H); 6.84-7.02 (m, 4H); 6.85-7.02 (m, 4H); 7.45 (d, 2H, *J* = 9 Hz); 7.86 (d, 1H, *J* = 3 Hz); 8.00 (d, 1H, *J* = 1 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.7; 141.3 (d, *J* = 4 Hz); 140.9 (d, *J* = 5 Hz); 136.4 (d, *J* = 3 Hz); 136.0 (d, *J* = 9 Hz); 132.4; 129.3; 128.5; 128.2; 115.0; 101.4 (d, *J* = 9 Hz); 99.8 (d, *J* = 5 Hz); 68.3; 62.7 (d, *J* = 7 Hz); 37.7 (d, *J* = 137 Hz); 36.8; 32.2; 29.9; 29.9; 29.8; 29.8; 29.6; 29.6; 29.5; 26.3; 22.9; 16.7; 16.6; 14.4.

IR (cm^{-1}): 3475, 3031, 2916, 2850, 1747, 1604, 1577, 1512, 1465, 1245, 1026, 960, 794.

Monophosphonate 1b A solution of diphosphonate (3.15 g, 5.00 mmol) in dry THF (75 mL) was stirred at 0 ºC under N_2 while ^{t}BuOK (505 mg, 4.50 mmol) was added carefully. After addition, the reaction mixture was stirred for 3 min. Then, 4-di(1-butyl)aminobenzaldehyde (933 mg, 4.00 mmol) in dry THF (5 mL) was added as quickly as possible. After 30-40 min, 75 mL of water, followed by 5 mL of an aqueous saturated solution of NH_4Cl, were added to quench the reaction. The mixture was extracted with DCM (3 x 75 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the crude mixture was purified by column chromatography (ethyl acetate / hexanes 1:2) to give **1b** as yellow oil. (1.39 g, 49%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.97 (t, 6H, *J* = 7.2 Hz); 1.28 (t, 6H, *J* = 7.2 Hz); 1.30-1.40 (m, 4H); 1.49-1.60 (m, 4H); 3.20-3.32 (m, 6H); 3.97-4.14 (m, 4H); 6.57 (d, 2H, *J* = 9 Hz); 6.83 (d, 1H, *J* = 16 Hz); 6.89 (d, 1H, *J* = 16 Hz); 7.39 (d, 2H, *J* = 9 Hz); 7.79 (d, 1H, *J* = 4 Hz); 7.98 (d, 1H, *J* = 2 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 148.5, 141.8 (d, *J* = 3.2 Hz), 140.7 (d, *J* = 6.4 Hz), 135.8 (d, *J* = 3.1 Hz), 135.0 (d, *J* = 9.6 Hz), 133.0, 128.6, 125.0, 123.5, 111.7, 101.6 (d, *J* = 7.2 Hz), 99.7 (d, *J* = 4.0 Hz), 62.7 (d, *J* = 7.2 Hz), 51.0, 37.6 (d, *J* = 137 Hz), 29.6, 20.5, 16.8 (d, *J* = 5.6 Hz), 14.3.

Monomer 2a: A solution of **1a** (6.25 g, 8.15 mmol) and 4-((trimethylsilyl)ethynyl)benzaldehyde (1.65 g, 8.15 mmol) in dry THF (85 mL) was stirred at 0ºC under N_2 while ^{t}BuOK (1.05 g, 9.38 mmol) was added carefully. After the addition, the reaction mixture was stirred for 30 min. Then, 30 mL of methanol followed by 1.50 g (10.8 mmol) of K_2CO_3 were added. The mixture was stirred at room temperature for 3 h. The reaction mixture was then poured into water and extracted with DCM (3 x 80 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the crude mixture was purified by column chromatography (hexanes / dichloromethane 9:1) to give **2a** as yellow solid. (3.36 g, 56%)

Mp: 148.0-150.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.88 (t, 3H, *J* = 6 Hz); 1.24-1.40 (m, 16H); 1.40-1.52 (m, 2H); 1.74-1.86 (m, 2H); 3.16 (s, 1H); 3.98 (t, 2H, *J* = 7 Hz); 6.89-7.02 (m, 5H); 7.20 (d, 1H, *J* = 16 Hz); 7.47 (d, 2H, *J* = 9 Hz); 7.49 (broad s, 4H); 8.05 (s, 2H)

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.8; 141.6; 140.1; 137.3; 136.6; 136.2; 132.8; 132.4; 131.8; 131.3; 129.3; 128.5; 128.2; 127.0; 122.0; 115.0; 100.7; 100.4; 83.8; 78.6; 68.4; 32.2; 29.9; 29.8; 29.6; 29.6; 29.5; 26.3; 22.9; 14.4.

IR (cm^{-1}): 3267, 3031, 2920, 2846, 2098, 1797, 1604, 1512, 1469, 1450, 1284, 1245, 1176, 1029, 956, 621.

MS (EI): (M^+) 742.2

Monomer 2b: A solution of **1b** (3.55 g, 5.00 mmol) and 4-((trimethylsilyl)ethynyl)-benzaldehyde (1.01 g, 5.00 mmol) in dry THF (85 mL) was stirred at 0ºC under N_2 while ^{t}BuOK (673 mg, 6.00 mmol) was added carefully. After addition, the reaction mixture was stirred for 30 min. Then, 30 mL of methanol followed by 1.50 g (10.8 mmol) of K_2CO_3 were added. The mixture was stirred at room temperature for 3 h. The reaction mixture was then poured into water and extracted with DCM (3 x 80 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the crude mixture was purified by column chromatography (hexanes / ethyl acetate 9:1) to give an orange solid. (2.53 g, 74%)

Mp: 125-128 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.97 (t, 6H, *J* = 7.2 Hz); 1.30-1.40 (m, 4H); 1.49-1.60 (m, 4H); 3.15 (s, 1H); 3.30 (t, 4H, *J* = 7.8 Hz); 6.62 (d, 2H, *J* = 9 Hz); 6.91 (d, 1H, *J* = 16 Hz); 6.93 (s, 2H); 7.19 (d, 1H, *J* = 16 Hz); 7.41 (d, 2H, *J* = 9 Hz); 7.49 (s, 4H); 8.04 (s, 2H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 148.4, 137.2, 136.3, 135.5, 132.8, 132.5, 131.8, 130.6, 128.9, 128.5, 126.7, 125.0, 123.6, 12.6, 111.5, 100.5, 100.1, 83.6, 78.2, 51.0, 29.4, 20.3, 14.0.

IR (cm^{-1}): 3031.0, 2954.1, 2872.1, 1602.7, 1519.8, 1367.0, 1182.1, 958.6, 753.8, 526.5.

MS (EI): (M^+) 685.1

Polymer 3a: A solution of **2a** (2.14 g, 2.88 mmol) in 18 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk flask, degassed and stirred under N_2 for 5 min at room temperature. The catalyst mixture, $PdCl_2(PPh_3)_2$ (10 mg, 14 μmol) and CuI (3 mg, 14 μmol), was added; the reaction was sealed and stirred at room temperature for 5 days. Methanol was added to precipitate the polymer, which was filtered off and washed three times with methanol to give a yellow solid. (1.53 g, 87%).

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-1 (br m, 3nH); 1-1.6 (br m, 18nH); 1.6-2 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.4-7.7 (m, 14nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.2; 139.7; 136.5; 132.4; 132.3; 129.2; 128.8; 128.5; 127.1; 122.4; 115.0; 100.8; 95.9; 89.6; 68.3; 32.2; 29.9; 29.7; 26.3; 22.9; 14.4.

IR (cm^{-1}): 3031, 2920, 2850, 2202, 1604, 1512, 1249, 1172, 956, 852; 813, 528.

Elem. Anal. C, 70.05%; H, 5.48%; I, 17.5% (calc. C, 70.12%; H, 6.44%; I, 20.58%)

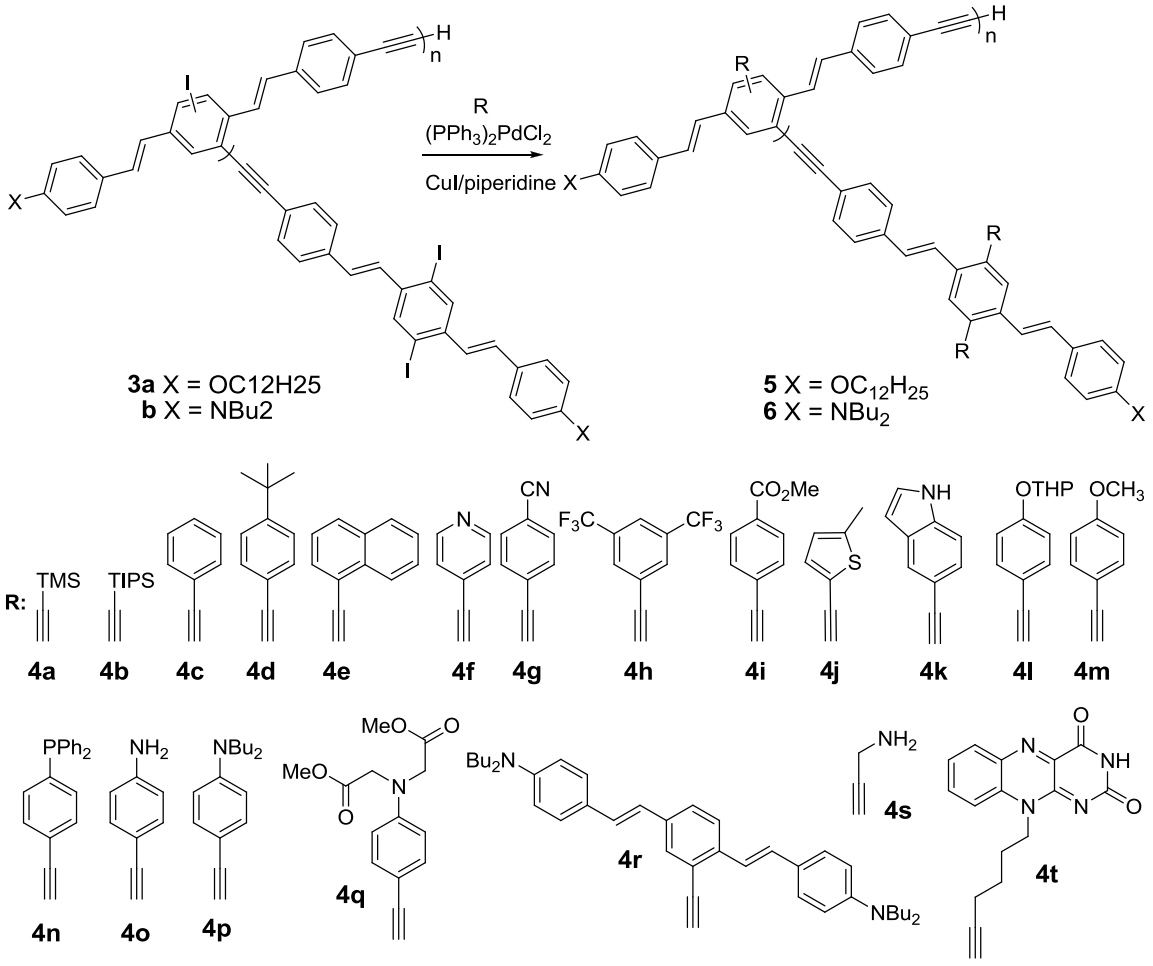
Polymer 3b: Same procedure as **3a**, using **2b** (2.40 g, 3.50 mmol) as monomer. Orange solid. (1.94 g, 81%).

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-1.15 (br m, 6nH); 1.20-1.45 (br m, 4nH); 1.45-1.70 (br m, 4nH); 2.95-3.40 (br m, 4nH); 6.40-6.70 (m, 2nH); 6.70-8.30 (m, 12nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 155.1; 148.2; 136.0; 131.8; 128.3; 126.7; 124.0; 122.1; 111.4; 100.6; 95.7; 89.0; 50.6; 29.3; 20.2; 14.0.

IR (cm^{-1}): 3033.8, 2952.8, 2869.9, 1602.7, 1517.9, 1367.4, 1184.21, 956.6, 804.3.

Elem. Anal. C, 67.90%; H, 5.73%; I, 21.80%; N, 2.35% (calc. C, 68.69%; H, 6.12%; I, 22.68%; N, 2.50%).



Scheme 3.4. Postfunctionalization of the polymer **3**.

Polymer 5a: A solution of polymer **3a** (92 mg, 0.15 mmol), $PdCl_2(PPh_3)_2$ (2 mg, 3 μmol) and CuI (0.5 mg, 3 μmol) in 2 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk flask, degassed and stirred under N_2 for 5 min at room temperature. The ethynyl derivative **4a** (98 mg, 1.0 mmol) was added; the reaction was then sealed and stirred at room

temperature overnight. Methanol was added to precipitate the polymer which was then filtered off and washed several times with methanol to give a yellow solid (85 mg, 97%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.1-0.5 (br m, 9nH); 0.75-0.95 (br m, 3nH); 0.95-1.55 (br m, 18nH); 1.7-2.1 (br m, 2nH); 3.8-4.2 (br m, 2nH); 6.0-8.5 (br m, 14nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.0; 137.4; 136.6; 131.9; 129.7; 128.0, 126.7, 123.1, 122.4, 114.7, 103.4, 100.3, 95.8, 89.8, 68.1, 32.0, 29.7, 29.5, 26.3, 26.1, 22.7, 14.1, 0.1.

IR (cm^{-1}): 3031, 2923, 2854, 2202, 2148, 1604, 1512, 1249, 1172, 960, 817, 759, 528.

Elem. Anal. C, 77.6%; H, 7.1%; I, 0.8% (calc. for complete reaction C, 83.90%; H, 8.59%; I, 0.00%) The low carbon value is quite typical for high carbon materials. Such effects have been observed in most cases of PPEs and relatives.

Polymer 5b: Same procedure as **5a**, using **4b** (182 mg, 0.999 mmol) as ethynyl derivative. (59 mg, 59%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-1 (br m, 3nH); 1-1.6 (br m, 39nH); 3.8-4.2 (br m, 2nH); 6.0-8.5 (br m, 14nH).

IR (cm^{-1}): 3030, 2957, 2940, 2855, 2201, 2143, 1604, 1506, 1456, 1250, 1245, 1172, 956, 817.

Elem. Anal. I, 0.1% (calc. for complete reaction I, 0.00%)

Polymer 5c: Same procedure as **5a**, using **4c** (102 mg, 0.999 mmol) as ethynyl derivative. (74 mg, 84%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.0-8.5 (br m, 19nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 158.9, 137.6, 136.1, 131.6, 129.9, 128.4, 128.1, 126.6, 123.4, 122.4, 114.5, 95.3, 89.9, 88.5, 68.0, 32.0, 29.7, 29.4, 26.2, 22.7, 14.2.

IR (cm^{-1}): 3031, 2923, 2850, 2202, 1604, 1512, 1249, 1172, 956, 813, 752, 524.

Elem. Anal. C, 85.03%; H, 6.44%; I, 0.2% (calc. for complete reaction C, 89.44%; H, 7.85%; I, 0.00%). The low carbon value is quite typical for high carbon materials. Such effects have been observed in most cases of PPEs and relatives.

Polymer 5d: Same procedure as **5a**, using **4d** (158 mg, 0.999 mmol) as ethynyl derivative. (92 mg, 95%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 27nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.0-8.5 (br m, 18nH).

IR (cm^{-1}): 3031, 2958, 2923, 2852, 2358, 2204, 1604, 1510, 1249, 1172, 958, 833, 815, 561, 528.

Elem. Anal. I, 0.4% (calc. for complete reaction I, 0.00%)

Polymer 5e: Same procedure as **5a**, using **4e** (68 mg, 0.45 mmol) as ethynyl derivative. (90 mg, 95%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.0-8.5 (br m, 21nH).

IR (cm^{-1}): 3041, 2921, 2849, 2198, 1604, 1508, 1250, 1172, 957.

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 158.9; 138.0; 136.5; 133.2; 132.1; 130.7, 130.4, 129.8, 128.2, 126.8, 126.5, 125.5, 122.3, 121.0, 114.6, 96.0, 93.4, 89.6, 68.1, 32.0, 29.7, 29.7, 26.1, 22.8, 14.2,

Elem. Anal. I, 0.1% (calc. for complete reaction I, 0.00%)

Polymer 5f: The TIPS protected form of the ethynyl derivative **4f**[8] (116mg, 0.450 mmol) was stirred in 3mL MeOH with two drops of DI H_2O and tetrabutylammonium fluoride trihydrate (425mg, 1.35 mmol) for 10 minutes at 50°C. The mixture was added to a solution of polymer **3a** (92 mg, 0.15 mmol) in 7 mL of a mixture of dry THF / piperidine 2:1 in a Schlenk flask. The mixture was degassed and stirred under N_2 for 5 min at room temperature. $PdCl_2(PPh_3)_2$ (2 mg, 3 μmol) and CuI (0.5 mg, 3 μmol) were added and the reaction was then sealed and stirred at room temperature overnight. Methanol was added to precipitate the polymer, which was then filtered off and washed three times with methanol to give a yellow solid (54 mg, 62%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.0-8.1 (br m, 16nH); 8.1-9.0 (br m, 2nH).

IR (cm^{-1}): 3030, 2920, 2852, 2205, 1604, 1590, 1507, 1468, 1246, 1170, 956, 800.

Elem. Anal. I, 1.8% (calc. for complete reaction I, 0.00%)

Polymer 5g: The TMS protected form of the ethynyl derivative **4g** (90mg, 0.45 mmol) was stirred in 2mL MeOH, 1mL THF and K_2CO_3 (75mg, 0.54 mmol) for 10 minutes. The mixture was added to a solution of polymer **3a** (92 mg, 0.15 mmol) in 7 mL of a mixture of dry THF / piperidine 2:1 in a Schlenk flask. The mixture was degassed and stirred under N_2 for 5 min at room temperature. $PdCl_2(PPh_3)_2$ (2 mg, 3 μmol) and CuI (0.5 mg, 3 μmol) were added and the reaction was then sealed and stirred at room temperature overnight. Methanol was added to precipitate the polymer, which was then filtered off and washed three times with methanol to give a yellow solid (82 mg, 90%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.0-8.5 (br m, 18nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.4; 137.2; 132.0; 129.3; 128.1; 127.4, 122.5, 118.5, 114.9, 111.4, 95.9, 94.1, 89.6, 68.1, 32.0, 29.7, 29.4, 26.1, 26.1, 22.7, 14.2.

IR (cm^{-1}): 3032, 2919, 2846, 2226, 2204, 1602, 1508, 1471, 1284, 1245, 958, 802.

Elem. Anal. I, 0.2% (calc. for complete reaction I, 0.00%)

Polymer 5h: Same procedure as **5g**, using TMS protected form of **4h**[8] (140 mg, 0.450 mmol) as ethynyl derivative. (55 mg, 52%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.0-8.5 (br m, 17nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.0; 138.0; 136.8; 132.1; 131.4; 129.2, 128.1, 126.9, 125.4, 124.8, 121.1, 114.8, 95.6, 91.9, 89.1, 68.1, 32.0, 29.7, 29.4, 26.1, 26.1, 22.7, 14.1.

IR (cm^{-1}): 3030, 2921, 2853, 2212, 1810, 1605, 1373, 1276, 1248, 1173, 1139, 957, 893, 815.

Elem. Anal. I, 0.5% (calc. for complete reaction I, 0.00%)

Polymer 5i: Same procedure as **5a**, using **4i**[9] (72 mg, 0.45 mmol) as ethynyl derivative. (74 mg, 77%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 5nH); 6.0-8.5 (br m, 18nH).

IR (cm^{-1}): 3031, 2925, 2852, 2205, 1723, 1602, 1510, 1471, 1434, 1304, 1273, 1245, 1173, 1017, 956, 854, 815.

Elem. Anal. I, 0.3% (calc. for complete reaction I, 0.00%)

Polymer 5j: Same procedure as **5g**, using TMS protected form of **4j** (87 mg, 0.45 mmol) as ethynyl derivative. (46 mg, 51%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 2.1-2.7 (br m, 3nH); 3.4-4.2 (br m, 2nH); 6.0-8.5 (br m, 16nH).

IR (cm^{-1}): 3029, 2919, 2852, 2197, 1602, 1507, 1457, 1245, 1170, 1025, 957, 856, 814.

Elem. Anal. I, 0.1% (calc. for complete reaction I, 0.00%)

Polymer 5k: Same procedure as **5a**, using **4k** (63 mg, 0.45 mmol) as ethynyl derivative. (83 mg, 89%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.0-8.5 (br m, 19nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.2, 138.0, 137.2, 136.0, 132.0, 129.4, 128.0, 125.8, 125.6, 125.0, 122.8, 122.4, 114.8, 103.2, 97.4, 86.1, 68.0, 31.9, 29.7, 29.3, 26.1, 22.7, 14.2.

IR (cm^{-1}): 3425, 3030, 2919, 2851, 2198, 1603, 1508, 1464, 1307, 1250, 1172, 957, 815.

Elem. Anal. I, 1.1% (calc. for complete reaction I, 0.00%)

Polymer 5l: Same procedure as **5a**, using **4l**[10] (91 mg, 0.45 mmol) as ethynyl derivative. (88 mg, 86%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.2.0 (br m, 24nH); 3.4-4.2 (br m, 6nH); 5.3-5.6 (br m, 1nH); 6.0-8.5 (br m, 16nH).

IR (cm^{-1}): 3030, 2921, 2852, 2206, 1602, 1507, 1240, 1172, 1121, 1111, 1037, 962, 919, 831, 814.

Elem. Anal. I, 0.1% (calc. for complete reaction I, 0.00%)

Polymer 5n: Same procedure as **5a**, using **4n** (128 mg, 0.450 mmol) as ethynyl derivative. (104 mg, 90%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 2nH); 6.0-8.5 (br m, 28nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.3, 137.9, 134.0, 132.1, 131.4, 129.6, 129.3, 128.3, 128.7, 127.0, 122.7, 114.9, 95.8, 88.7, 68.1, 31.9, 29.7, 29.4, 26.2, 22.7, 14.2.

IR (cm^{-1}): 3049, 2919, 2851, 2176, 2102, 1899, 1810, 1627, 1604, 1509, 1433, 1393, 1247, 1172, 1116, 1094, 957, 852, 823.

Elem. Anal. I, 3.8% (calc. for complete reaction I, 0.00%)

Polymer 5o: Same procedure as **5a**, using **4b** (117 mg, 0.999 mmol) as ethynyl derivative. (82 mg, 89%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.5 (br m, 18nH); 1.7-2.0 (br m, 2nH); 3.4-4.2 (br m, 4nH); 6.0-8.3 (br m, 18nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 158.8, 146.6, 137.5, 133.0, 131.8, 129.9, 128.2, 126.8, 123.7, 122.5, 114.7, 112.5, 96.1, 90.0, 86.4, 68.2, 32.3, 29.8, 29.5, 26.3, 22.9, 14.4.

IR (cm^{-1}): 3031, 2923, 2850, 2202, 1604, 1512, 1249, 1172, 956, 813, 752, 524.

Elem. Anal. C, 85.03%; H, 6.44%; I, 0.2% (calc. for complete reaction C, 89.44%; H, 7.85%; I, 0.00%). The low carbon value is quite typical for high carbon materials. Such effects have been observed in most cases of PPEs and relatives.

Polymer 5p: Same procedure as **5a**, using **4p**[8] (230 mg, 1.0 mmol) as ethynyl derivative. (91 mg, 85%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.70-1.05 (br m, 9nH); 1.05-1.50 (br m, 22nH); 1.50-1.70 (br m, 4nH); 1.70-1.90 (br m, 2nH); 3.0-3.5 (br m, 4nH); 3.6-4.2 (br m, 2nH); 6.0-8.5 (br m, 18nH)

IR (cm^{-1}): 3406, 3031, 2923, 2854, 2194, 1604, 1515, 1249, 1172, 960, 813, 524.

Elem. Anal. C, 84.66%; H, 7.34%; N, 2.02%; I, 0.3% (calc. for complete reaction C, 86.98%; H, 8.84%; N, 1.95%; I, 0.00%) The low carbon value is quite typical for high carbon materials. Such effects have been observed in most cases of PPEs and relatives.

Polymer 5r: Same procedure as **5a**, using **4r** (284 mg, 0.450 mmol) as ethynyl derivative. (129 mg, 83%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.70-1.05 (br m, 15nH); 1.05-1.90 (br m, 36nH); 2.9-3.5 (br m, 8nH); 3.6-4.2 (br m, 2nH); 6.0-8.5 (br m, 30nH)

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 159.2, 148.0, 138.1, 136.4, 131.9, 130.1, 128.7, 127.2, 127.9, 126.9, 124.4, 122.4, 121.5, 114.7, 111.6, 96.3, 95.1, 92.6, 89.4, 68.0, 50.7, 32.0, 29.7, 29.4, 26.1, 22.7, 20.3, 14.2, 14.0

IR (cm^{-1}): 3029, 2954, 2924, 2853, 2200, 1603, 1518, 1462, 1366, 1251, 1184, 957, 815, 802.

Elem. Anal. I, 0.1% (calc. for complete reaction I, 0.00%)

Polymer 5s: Same procedure as **5a**, using **4s** (55 mg, 1.0 mmol) as ethynyl derivative. (71 mg, 88%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.55 (br m, 18nH); 1.6-2.1 (br m, 5nH); 2.2-2.6 (br m, 2nH); 3.8-4.2 (br m, 2nH); 6.0-8.5 (br m, 19nH).

IR (cm^{-1}): 3386, 3031, 2923, 2852, 2356, 2206, 1604, 1469, 1245, 1172, 1026, 960, 638, 503.

Elem. Anal. I, 0.7% (calc. for complete reaction I, 0.00%)

Polymer 5t: Same procedure as **5a**, using **4t**[11] (284 mg, 0.450 mmol) as ethynyl. Yellow solid (76 mg, 70%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-0.95 (br m, 3nH); 0.95-1.55 (br m, 18nH); 1.9-2.1 (br m, 2nH); 2.1-2.4 ((br m, 2nH); 2.4-2.5 (br m, 2 nH); 2.5-2.6 (br m, 2nH); 3.8-4.2 (br m, 2nH); 4.5-4.8 (br m, 2nH); 6.0-8.3 (br m, 23 nH); 8.6-8.8 (br m, 1nH).

IR (cm^{-1}): 3471, 3257, 3157, 3105, 3029, 2921, 2850, 2812, 2206, 1710, 1654, 1575, 1541, 1508, 1463, 1350, 1253, 1172, 958, 858, 669, 590, 464.

Polymer 6a: A solution of polymer **3b** (150 mg, 0.268 mmol), $PdCl_2(PPh_3)_2$ (2 mg, 3 μmol) and CuI (0.5 mg, 3 μmol) in 2 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk flask, degassed and stirred under N_2 for 5 min at room temperature. The ethynyl derivative **4a** (98 mg, 1.0 mmol) was added. The reaction was then sealed and stirred at room temperature overnight. Methanol was added to precipitate the polymer which was then filtered off and washed several times with methanol to give a yellow solid (126 mg, 88%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.2-0.5 (br m, 9nH); 0.85-1.05 (br m, 6nH); 1.20-1.45 (br m, 4nH); 1.45-1.70 (br m, 4nH); 2.95-3.40 (br m, 4nH); 6.40-6.70 (m, 2nH); 6.70-8.30 (m, 12nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 147.9, 238.8, 137.6, 135.9, 135.5, 133.8, 131.9, 131.0, 128.7, 128.4, 126.6, 124.3, 122.1, 121.5, 120.0, 111.5, 103.5, 100.2, 95.6, 89.7, 50.6; 29.3; 20.2; 14.0, 0.2.

IR (cm^{-1}): 3031, 2956, 2870, 2148, 1604, 1519, 1367, 1184, 958, 856, 526.

Elem. Anal. I, 0.3% (calc. for complete reaction I, 0.00%)

Polymer 6b: Same procedure as **6a**, using **4b** (182 mg, 0.999 mmol) as ethynyl derivative. Orange solid (153 mg, 93%).

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.80-1.02 (br m, 6nH); 1.06-1.43 (m, 25nH); 1.45-1.70 (br m, 4nH); 3.00-3.40 (br m, 4nH); 6.40-6.70 (m, 2nH); 7.00-8.00 (m, 12nH).

IR (cm^{-1}): 3031.9, 2954.7, 2864.1, 2146.6, 1604.7, 1519.8, 1184.2, 958.6, 667.3.

Elem. Anal. I, 0.2% (calc. for complete reaction I, 0.00%)

Polymer 6c: Same procedure as **6a**, using **4c** (102 mg, 0.999 mmol) as ethynyl derivative. Orange solid (130 mg, 91%).

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-1.15 (br m, 6nH); 1.20-1.45 (br m, 4nH); 1.45-1.70 (br m, 4nH); 2.95-3.40 (br m, 4nH); 6.40-6.70 (m, 2nH); 6.70-8.30 (m, 17nH).

IR (cm^{-1}): 3030.0, 2954.7, 2869.9, 1602.7, 1519.8, 1367.4, 1182.3, 958.6, 754.1, 688.5, 526.5.

Elem. Anal. I, 0.8% (calc. for complete reaction I, 0.00%)

Polymer 6h: Same procedure as **5g**, using **3b** as the starting polymer (150 mg, 0.268 mmol) and TMS protected form of **4h**[8] (280 mg, 0.900 mmol) as ethynyl derivative. Red solid (176 mg, 98%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-1.15 (br m, 6nH); 1.20-1.45 (br m, 4nH); 1.45-1.70 (br m, 4nH); 2.95-4.40 (br m, 4nH); 6.40-6.80 (m, 2nH); 6.70-8.30 (m, 15nH).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 155.0, 148.7, 131.8, 131.4, 128.3, 126.5, 121.2, 111.4, 88.0, 50.6; 29.3; 20.2; 14.0.

IR (cm^{-1}): 3031.9, 2954.7, 2873.7, 2210.3, 1602.7, 1519.8, 1398.3, 1371.3, 1278.7, 1182.3, 1137.9, 958.6, 893.0, 698.2, 526.5.

Elem. Anal. I, 0.4% (calc. for complete reaction I, 0.00%)

Polymer 6m: Same procedure as **6a**, using **4m** (132 mg, 0.999 mmol) as ethynyl derivative. Orange solid (142 mg, 94%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-1.15 (br m, 6nH); 1.20-1.45 (br m, 4nH); 1.45-1.70 (br m, 4nH); 2.95-3.40 (br m, 4nH); 3.40-3.80 (br m, 3nH); 6.00-8.00 (m, 18nH).

IR (cm^{-1}): 3031.9, 2954.7, 2869.9, 2204.5, 1604.7, 1514.0, 1247.8, 1182.3, 958.6, 829.3, 806.2, 532.3.

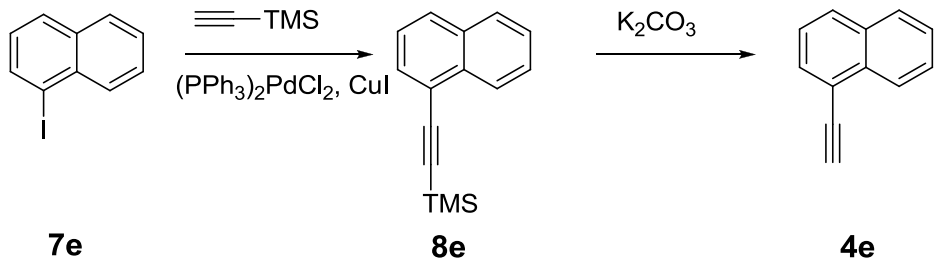
Elem. Anal. I, 0.3% (calc. for complete reaction I, 0.00%)

Polymer 6q: Same procedure as **6a**, using **4q** (261 mg, 0.999 mmol) as ethynyl derivative. Orange solid (137 mg, 74%).

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.75-1.15 (br m, 6nH); 1.20-1.45 (br m, 4nH); 1.45-1.70 (br m, 4nH); 2.95-3.40 (br m, 4nH); 3.50-3.85 (m, 4nH); 3.90-4.40 (m, 6nH); 6.40-6.80 (m, 2nH); 6.70-8.30 (m, 15nH).

IR (cm^{-1}): 3031.9, 2950.1, 2871.8, 2200.6, 1747.4, 1604.7, 1519.8, 1182.3, 960.5, 813.9, 528.5.

Elem. Anal. I, 0.3% (calc. for complete reaction I, 0.0%)



Scheme 3.5. Synthesis of **4e.**

Compound 8e: A solution of 1-iodonapthalene (1.37 g, 5.39 mmol), $PdCl_2(PPh_3)_2$ (38 mg, 54 μmol) and CuI (10 mg, 54 μmol) in 20 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk tube, degassed and stirred under N_2 for 5 min at room temperature. Trimethylsilylacetylene (2.64g, 27.0 mmol) was added; the reaction was then sealed and stirred at 25°C overnight. The crude mixture was dissolved in 100 ml dichloromethane and washed with 100 mL H_2O, with 100 mL 10% HCl solution and with 100mL H_2O. The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The crude mixture was purified by column chromatography (hexanes) providing a colorless oil. (0.80 g, 67%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.52 (s, 9H); 7.48 (t, 1H, *J* = 8 Hz); 7.60 (t, 1H, *J* = 8 Hz); 7.71 (t, 1H, *J* = 7 Hz); 7.85-7.92 (m, 3H); 8.56 (d, 1H, *J* = 8 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 133.8; 133.5; 131.2; 129.4; 128.7; 127.3; 126.8; 126.6; 125.5; 121.2; 103.7; 99.8; 0.6.

IR (cm^{-1}): 3056, 2958, 2894, 2789, 2482, 2146, 1932, 1812, 1704, 1585, 1503, 1392, 1248, 1154, 1074, 1012, 801.

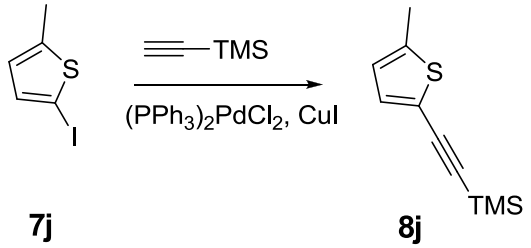
Compound 4e: 8e (0.70 g, 3.1 mmol) was stirred in mixture of 12mL THF and 20mL THF in the presence of K_2CO_3 (1.00 g, 7.23 mmol) for 3 hours. The reaction mixture was poured into

50mL dichloromethane and the combined organic layer was washed with water (3 x 80mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo, providing a red oil. (0.26 g, 55%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 3.6 (s, 1H); 7.49 (t, 1H, *J* = 8 Hz); 7.60 (t, 1H, *J* = 8 Hz); 7.71 (t, 1H, *J* = 7 Hz); 7.85-7.93 (m, 3H); 8.53 (d, 1H, *J* = 8 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 133.9; 133.5; 131.7; 129.7; 128.7; 127.4; 126.9; 126.5; 125.5; 129.2; 103.7; 82.3.

IR (cm^{-1}): 3286, 3056, 2924, 2099, 1934, 1815, 1703, 1586, 1508, 1391, 1335, 1265, 1012, 857, 799.



7j **8j**

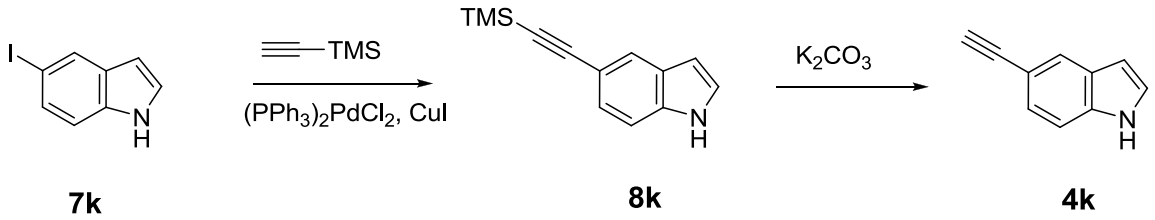
Scheme 3.6. Synthesis of **8j** (TMS-protected form of **4j**).

Compound 8j: A solution of 2-iodo-5-methylthiophene (1.08 g, 4.92 mmol), $PdCl_2(PPh_3)_2$ (34 mg, 0.050 mmol) and CuI (9 mg, 0.05 mmol) in 20 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk tube, degassed and stirred under N_2 for 5 min at room temperature. Trimethylsilylacetylene (2.36 g, 24.1 mmol) was added, the reaction was then sealed and stirred at 25°C overnight. The crude mixture was dissolved in 50 ml dichloromethane and washed with H_2O (3 x 50 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The crude mixture was purified by column chromatography (hexanes) providing a colorless oil. (0.70 g, 75%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.22 (s, 9H); 2.43 (s, 3H); 6.58 (d, 1H, *J* = 4 Hz); 7.02 (d, 1H, *J* = 4 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 142.4; 133.2; 125.4; 120.9; 98.2; 97.9; 29.9; 0.2.

IR (cm^{-1}): 3072, 2957, 2920, 2856, 2143, 1745, 1593, 1537, 1455, 1247, 1176, 1153, 1133, 854.



7k **8k** **4k**

Scheme 3.7. Synthesis of **4k.**

Compound 8k: A solution of 5-iodoindole (1.32 g, 5.43 mmol), $PdCl_2(PPh_3)_2$ (38 mg, 0.054 mmol) and CuI (10 mg, 0.054 mmol) in 20 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk tube, degassed and stirred under N_2 for 5 min at room temperature.Trimethylsilylacetylene (2.66 g, 27.1 mmol) was added, the reaction was then sealed and stirred at 40°C overnight. The crude mixture was dissolved in 50 mL dichloromethane and washed with H_2O (3 x 50 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The crude mixture was purified by column chromatography (hexanes / ethyl acetate 4:1) providing a yellow oil. (0.85 g, 73%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.35 (s, 9H); 6.51-6.53 (m, 1H); 7.08 (t, 1H, *J* = 3 Hz); 7.20 (d, 1H, *J* = 10 Hz); 7.36 (d, 1H, *J* = 8 Hz); 7.91 (s, 1H); 8.12-8.26 (br s. 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 135.9; 127.9, 126.1, 125.7, 125.4, 114.3, 111.5, 107.6, 103.0, 91.7, 0.6.

IR (cm^{-1}): 3410, 3105, 2952, 2895, 2145, 1616, 1466, 1415, 1311, 1247, 1145, 1089, 942, 840, 802.

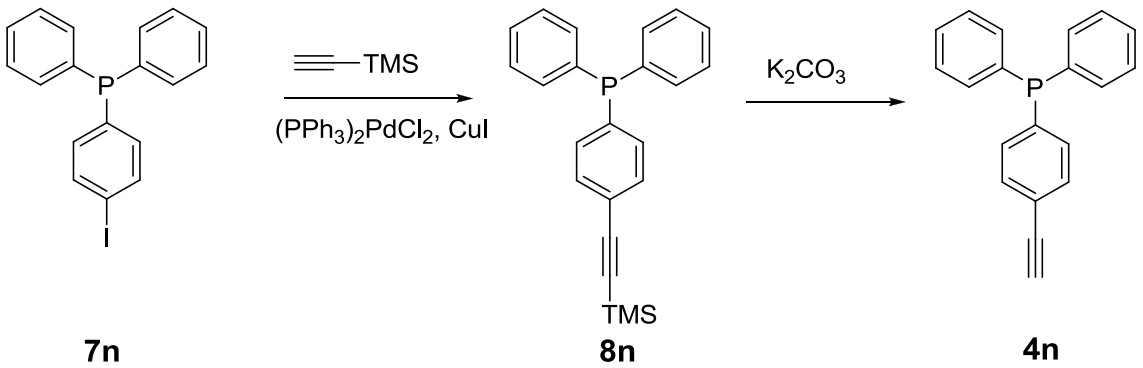
Compound 4k: 8k (0.43 g, 2.0 mmol) was stirred in mixture of 8mL THF and 12mL THF in the presence of K_2CO_3 (1.30 g, 9.40 mmol) for 3 hours. The reaction mixture was poured into 50mL dichloromethane and the combined organic layer was washed with water (3 x 50mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo, providing a brown solid. (0.21 g, 74%).

Mp: 65.0-66.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.35 (s, 9H); 6.51-6.53 (m, 1H); 7.08 (t, 1H, *J* = 3 Hz); 7.20 (d, 1H, *J* = 10 Hz); 7.36 (d, 1H, *J* = 8 Hz); 7.91 (s, 1H); 8.12-8.26 (br s. 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 135.9; 127.9; 126.1; 125.7; 125.6; 113.3; 111.5; 103.0; 85.7; 75.2.

IR (cm^{-1}): 3427, 3268, 3129, 3108, 2956, 2952, 2851, 2099, 1873, 1735, 1610, 1463, 1413, 1340, 1310, 1242, 1087, 1065, 889, 809.



Scheme 3.8. Synthesis of **4n.**

Compound 8n: A solution of **7n**[12] (1.29 g, 3.32 mmol), $PdCl_2(PPh_3)_2$ (23 mg, 0.033 mmol) and CuI (6 mg, 0.03 mmol) in 20 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk tube, degassed and stirred under N_2 for 5 min at room temperature. Trimethylsilylacetylene (1.63 g, 16.6 mmol) was added; the reaction was then sealed and stirred at 25°C overnight. The crude mixture was dissolved in 50 mL dichloromethane and washed with H_2O (3 x 50 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The crude mixture was purified by column chromatography (hexanes / ethyl acetate 49:1) providing a colorless solid. (0.83 g, 70%).

Mp: 67.5-68.0 ºC.

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.29 (s, 9H); 7.26 (t, 2H, *J* = 8 Hz); 7.29-7.39 (m, 10H); 7.45 (d, 2H, *J* = 8 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 138.5 (d, *J* = 12 Hz); 136.9 (d, *J* = 11 Hz); 134.1 (d, *J* = 20 Hz); 133.6 (d, *J* = 19 Hz); 132.1 (d, *J* = 7 Hz); 129.2; 128.9 (d, *J* = 7 Hz); 123.6; 105.1; 95.7; 0.3.

IR (cm^{-1}): 3066, 3050, 2962, 2951, 2896, 2153, 1949, 1918, 1652, 1587, 1473, 1430, 1247, 1218, 1081, 1016, 857, 826, 819.

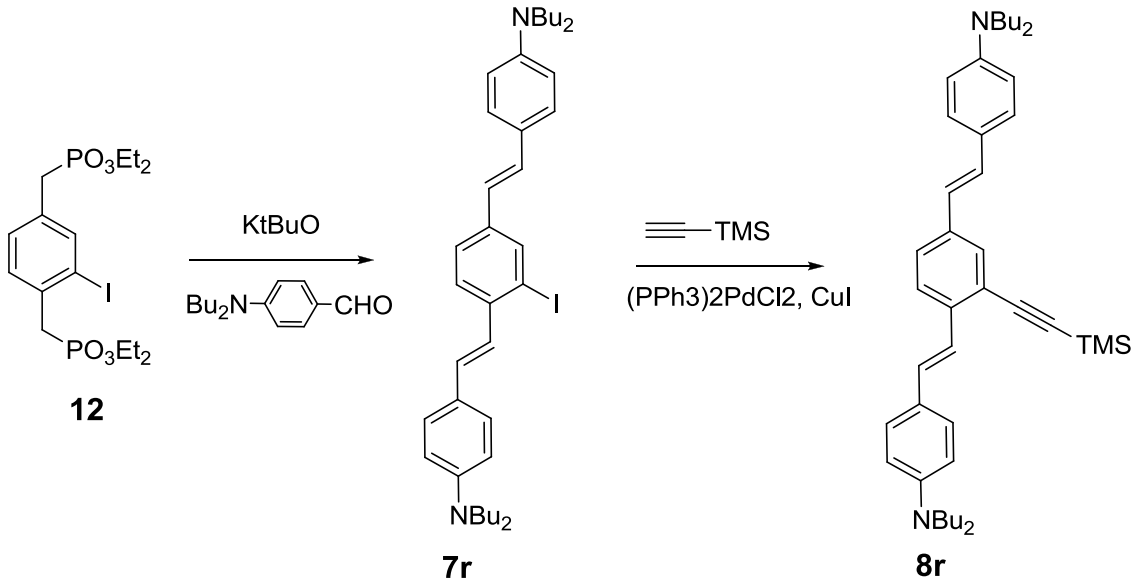
Compound 4n: 8n (0.55 g, 1.5 mmol) was stirred in mixture of 8mL THF and 12mL THF in the presence of K_2CO_3 (1.00 g, 7.23 mmol) for 3 hours. The reaction mixture was poured into 50mL dichloromethane and the combined organic layer was washed with water (3 x 50mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo, providing a colorless solid. (0.33 g, 75%).

Mp: 66.0-67.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 3.15 (s, 1H); 7.32 (t, 2H, *J* = 8 Hz); 7.35-7.42 (m, 10H); 7.50 (d, 2H, *J* = 8 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 139.1 (d, *J* = 12 Hz); 136.8 (d, *J* = 11 Hz); 134.2 (d, *J* = 20 Hz); 133.7 (d, *J* = 19 Hz); 132.3 (d, *J* = 7 Hz); 129.3; 129.0 (d, *J* = 7 Hz); 122.6; 83.7; 78.7.

IR (cm^{-1}): 3288, 3066, 3048, 3026, 2104, 1930, 1582, 1484, 1433, 1381, 1239, 1154, 1104, 1087, 1016, 1000, 843, 833.



Scheme 3.9. Synthesis of **8r** (TMS-protected form of **4r**).

Compound 7r: A solution of diphosphonate **12** (1.00 g, 2.04 mmol) in dry THF (40 mL) was stirred at 25ºC under N_2 while ^{t}BuOK (0.412 g, 4.08 mmol) was added carefully. After addition, the reaction mixture was stirred for 3 min. Then, 4-dibutylaminobenzaldehyde (0.86 g, 3.7 mmol) in dry THF (5 mL) was added as quickly as possible. After 30-40 min, 100 mL of water, followed by 5 mL of a saturated solution of NH_4Cl, were added to quench the reaction. The mixture was extracted with DCM (3 x 100 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and

the crude mixture was purified by column chromatography (hexane / dichloromethane 4:1) The product was isolated as an orange oil. (0.83 g, 61%).

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.98 (t, 12H, *J* = 7 Hz); 1.32-1.44 (m, 8H); 1.55-1.65 (m, 8H); 3.31 (t, 8H, *J* = 6 Hz); 6.60-6.70 (m, 4H); 6.75 (d, 1H, *J* = 16 Hz); 6.88-7.16 (m, 4H); 7.34-7.48 (m, 4H); 7.55 (d, 1H, *J* = 8 Hz); 7.96 (d, 1H, *J* = 2 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 148.3; 148.2; 139.0; 138.7; 137.1; 131.2; 129.7; 128.4; 128.2; 127.4; 126.0; 125.5; 124.6; 124.4; 121.8; 111.9; 101.1; 51.1; 29.8; 20.6; 14.3.

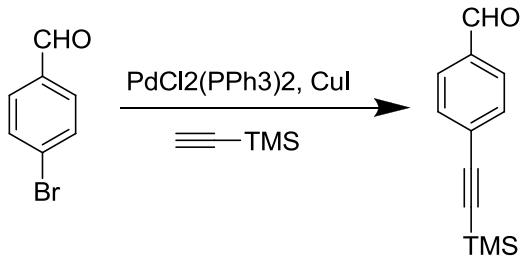
IR (cm^{-1}): 3072, 3029, 2952, 2927, 2869, 1602, 1519, 1396, 1367, 1184, 958, 842, 819, 522.

Compound 8r: A solution of **7r** (0.60 g, 0.90 mmol), $PdCl_2(PPh_3)_2$ (6 mg, 9 μmol) and CuI (2 mg, 9 μmol) in 20 mL of a mixture of dry THF / piperidine 2:1 was prepared in a Schlenk tube, degassed and stirred under N_2 for 5 min at room temperature.Trimethylsilylacetylene (0.44 g, 4.5 mmol) was added, the reaction was then sealed and stirred at 40°C overnight. The crude mixture was dissolved in 50 mL dichloromethane and washed with H_2O (3 x 50 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The crude mixture was purified by column chromatography (hexane / dichloromethane 4:1) providing a yellow oil. (0.37 g, 64%)

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 0.34 (s, 9H); 1.03 (t, 12H, *J* = 7 Hz); 1.37-1.46 (m, 8H); 1.57-1.71 (m, 8H); 3.27-3.40 (m, 8H); 6.58-6.68 (m, 4H); 6.78 (d, 1H, *J* = 16 Hz); 6.98-7.14 (m, 2H); 7.32-7.48 (m, 6H); 7.55 (d, 1H, *J* = 2 Hz); 7.60 (d, 1H, *J* = 8 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 148.1; 148.0; 138.4; 136.4; 130.4; 129.9; 129.1; 128.2; 128.0; 126.5; 126.4; 124.9; 124.6; 124.3; 122.7; 121.6; 121.5; 111.8; 104.5; 98.8. 51.0; 29.7; 20.6; 14.3; 0.4.

IR (cm^{-1}): 3074, 3031, 2958, 2869, 2146, 1730, 1602, 1519, 1396, 1367, 1184, 1024, 956, 817, 574, 516.



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Scheme 3.10. Synthesis of 4-(trimethylsilylethynyl)benzaldehyde**.**

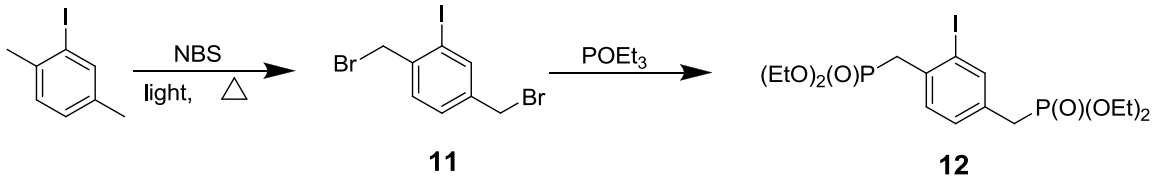
Compound 10: A solution of 4-bromobenzaldehyde (3.29g, 17.8 mmol), $PdCl_2(PPh_3)_2$ (125 mg, 0.178 mmol) and CuI (33 mg, 0.18 mmol) in 20 mL of a mixture of dry THF / triethylamine 2:1 was prepared in a bomb tube, degassed and stirred under N_2 for 5 min at room temperature.Trimethylsilylacetylene (8.74g, 88.9 mmol) was added, the reaction was then sealed and stirred at 65°C overnight. The crude mixture was dissolved in 100 mL dichloromethane and washed with 100 mL H_2O, 100 mL 10% HCl solution and with 100mL H_2O. The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The crude mixture was purified by column chromatography (hexanes / dichloromethane 3:2) providing a colorless solid. (3.16g, 86%)

Mp: 96.5-98.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 7.54-7.38 (m, 3H); 7.54-7.57 (m, 2H); 7.66 (d, 2H, *J* = 8 Hz); 7.86 (d, 2H, *J* = 14 Hz); 10.00 (s, 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 191.7; 135.6; 132.3; 132.0; 129.8; 129.2; 128.7; 122.7; 93.7; 88.8.

IR (cm^{-1}): 3359, 3047, 2846, 2742, 2214, 1948, 1701, 1600, 1384, 1207, 813, 752.



Scheme 3.11. Synthesis of the precursor **12.**

Compound 11: 2-iodo-para-xylene (30.0 g, 129 mmol) and N-bromosuccinimide (52.91 g, 297.3 mmol) were placed in a round bottom flask and 750 mL of $CHCl_3$ were added. The reaction was refluxed under the light of one 120 W sunlamp for 3 h. After this time, the mixture was allowed to cool to room temperature and decolorized with an aqueous solution of sodium sulfite. The organic phase was washed three times with water (3 x 250 mL) and the combined organic layers were dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the crude mixture was purified by column chromatography (hexanes / dichloromethane 9:1) to provide a colorless solid. (21.65 g, 43%)

Mp: 112.0-113.5 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 4.37 (s, 1H); 4.55 (s, 1H); 7.36 (dd, 1H, *J* = 2 Hz, 8Hz); 7.44 (d, 1H, *J* = 8 Hz); 7.88 (d, 1H, 2 Hz).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz): 140.3; 140.3; 139.7; 130.6; 129.5; 99.9; 38.0; 31.0.

IR (cm^{-1}): 3899, 3028, 2974, 2846, 2630, 2434, 2230, 1982, 1905, 1786, 1593, 1485, 1431, 1396, 1226, 1199, 894, 833, 632.

Compound 12: Compound **11** (5.50 g, 14.1 mmol) was dissolved in 25 mL of triethylphosphite and the mixture was stirred at 140 ºC for 4 h under reflux. Hexanes were added and the flask was left in the freezer until a transparent oil remained in a different phase, becoming a white solid

afterwards. The precipitate was filtered and washed with hexanes to provide a colorless solid, (5.25 g, 74%)

Mp: 43.5-45.0 ºC

^{1}H-NMR, $CDCl_3$ (δ, 300 MHz): 1.25 (t, 12H, *J* = 7 Hz), 3.05 (d, 2H, *J* = 20 Hz); 3.38 (d, 2H, 20 Hz); 4.02 (m, 8H); 7.25 (d, 1H, *J* = 8 Hz); 7.40 (m, 1H); 7.77 (s, 1H).

^{13}C-NMR, $CDCl_3$ (δ, 75 MHz):140.8 (d, *J* = 6Hz); 134.3 (dd, *J* = 4Hz, 9Hz); 132.6 (dd, *J* = 4Hz, 9Hz); 130.7 (dd, *J* = 3Hz, 6Hz); 130.0 (d, *J* = 3Hz, 6Hz); 101.3 (dd, *J* = 4Hz, 9Hz); 62.4 (dd, *J* = 3Hz, 6Hz); 38.1 (d, *J* = 138Hz); 32.8 (d, *J* = 138Hz); 16.3 (d, *J* = 6Hz).

IR (cm^{-1}): 2977, 2908, 2441, 2264, 2191, 1917, 1778, 1747, 1596, 1485, 1388, 1226, 1053, 848, 590.

3.3.3 Supplemental Data

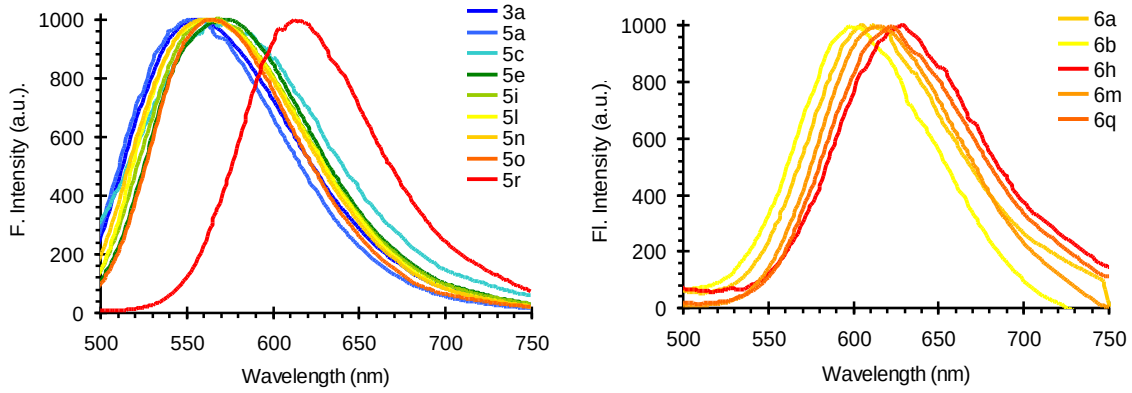


Figure 3.8. Solid state fluorescence of the polymers shown in Figure

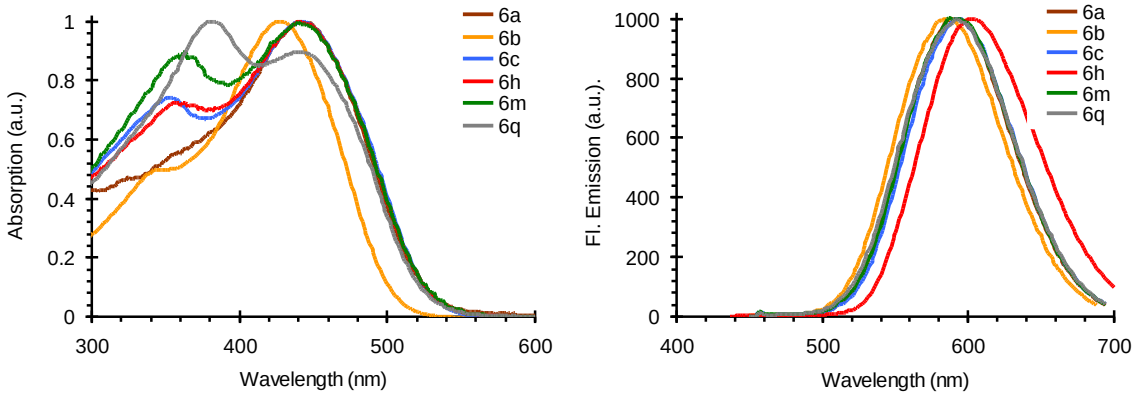


Figure 3.9. Normalized absorption and emission of polymers **6a-q**.

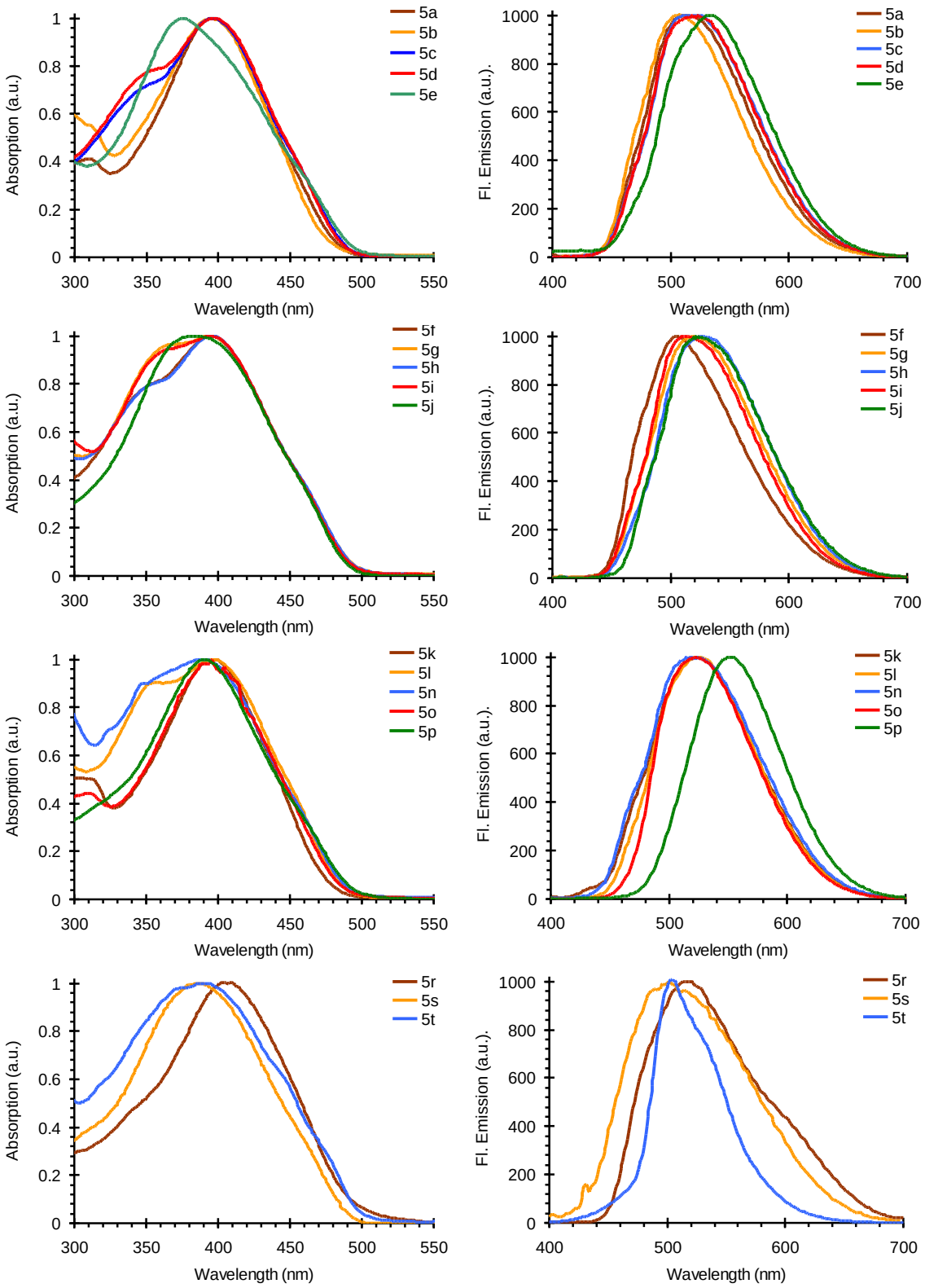


Figure 3.10. Normalized absorption and emission of polymers **5a-t**.

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4. The fluorescence lifetime measurements were taken slightly off the maxima, at 480 and 620 nm, respectively, to ensure a single-band fluorescence at those wavelengths.

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CHAPTER 4

CONCLUSION AND FUTURE DIRECTIONS

4.1 Discussion

This thesis demonstrates the potential for the use of hyperbranched conjugated polymers in sensory and other applications. A hyperbranched conjugated polymer was shown to have red-shifted absorbance and emission spectra in comparison to monomer and linear polymer models, further opening the door toward sensing applications that require red-absorbing or red-emitting fluorophores. Additionally, a hyperbranched conjugated polymer was shown to have increased rates of energy transfer in comparison to a similar linear polymer, being approximately twice as efficiently quenched by paraquat as the linear polymer.

The hyperbranched polymers described can act as universal conjugated platforms. A single large batch of iodine-substituted polymer can be postfunctionalized by an endless variety of alkynes using Pd-catalyzed Sonogashira coupling, reducing synthetic costs and thereby opening up countless possibilities. The hyperbranched conjugated polymers described were substituted with >95% efficiency, providing a library of 24 different derivative polymers. Spectroscopic studies of the derivatives make clear that functionalization affects the electronic and optical properties of the polymer backbones, including absorbance maxima, emission maxima, and quantum yield. Emission maxima range from 505 to 602 nm. Interestingly, the position and distribution of electron-donating dibutylamino groups on the polymeric backbone changes the optical properties of the hyperbranched polymers. Additionally, the pre-functional styryl groups introduced in the first step of the synthesis can have a strong influence on the electronic properties of the polymers. In this regard, it would be of great interest to introduce this

functionality in a later synthetic step to gain control of the styryl functionality once the polymerization reaction is completed. The ability to alter the electronic and optical properties of the polymers in both prefunctionalization and postfunctionalization suggests great potential for the use of hyperbranched conjugated polymer in organic electronics, sensory applications and supramolecular chemistry.

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